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A further note on the presentation of chemical analyses of minerals.[1]

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SUPPOSE that in the study of a mineral we have determined the cell-dimensions and the density, and made a chemical analysis. From these we can readily calculate the empirical unit-cell contents, which will usually approach integral values and so suggest a probable formula.

But the calculated empirical unit-cell contents, being based on chemical and physical data subject to experimental error, will be subject to numerous sources of error, and in any serious study it is very desirable to have some rough idea of the probable limits of error. Unfortunately, this is a matter of considerable complexity, but the following suggestions may be of assistance, though they will doubtless be considerably improved on.

The 'probable error' of the density and cell-dimensions can usually be assessed without much difficulty, but the errors of the chemical analysis are by no means easy to estimate.

Considering first the errors of the physical data, we may take as an example a monoclinic mineral for which we have the experimental cell-dimensions $(a\pm\delta a)$ Å., $(b\pm\delta b)$ Å., $(c\pm\delta c)$ Å., $(\beta\pm\delta\beta)^\circ$, and specific gravity[2] $D\pm\delta D$. The cell-weight, $W = abcD\sin\beta$, will be subject to an error δW that may reasonably be assessed, assuming the errors δa,

[1] M. H. Hey, Min. Mag., 1939, vol. 25, p. 402.

[2] The specific gravity must, of course, be corrected for all known impurities, including hygroscopic water; and due allowance must be made for uncertainties in the amount of impurity and in the uniformity of its distribution when assessing the probable error in the specific gravity, δD.

δb, δc are truly independent, by squaring and adding[1] the several rel
tive errors $\delta a/a$, $\delta b/b$, $\delta c/c$, $\{\sin\beta-\sin(\beta-\delta\beta)\}/\sin\beta$, and $\delta D/D$:

$$\left(\frac{\delta W}{W}\right)^2=\left(\frac{\delta a}{a}\right)^2+\left(\frac{\delta b}{b}\right)^2+\left(\frac{\delta c}{c}\right)^2+(\delta\beta\cot\beta)^2+\left(\frac{\delta D}{D}\right)^2 \quad . \quad .$$

If, however, the errors δa, δb, δc, are not independent, we shall ha
a larger value for δW, since then:

$$\left(\frac{\delta W}{W}\right)^2=\left(\frac{\delta a}{a}+\frac{\delta b}{b}+\frac{\delta c}{c}\right)^2+(\delta\beta\cot\beta)^2+\left(\frac{\delta D}{D}\right)^2 \quad . \quad . \quad .$$

In a tetragonal, hexagonal, or cubic mineral the errors in the two c
three equal cell-dimensions are obviously not independent, and

$$\left(\frac{\delta W}{W}\right)^2=\left(\frac{2\delta a}{a}\right)^2+\left(\frac{\delta c}{c}\right)^2+\left(\frac{\delta D}{D}\right)^2$$

for tetragonal and hexagonal minerals, or

$$\left(\frac{3\delta a}{a}\right)^2+\left(\frac{\delta D}{D}\right)^2$$

for cubic minerals.

Measurements of unit-cell dimensions are subject to error from severa
sources, some of which, such as errors in the measurement of distance
between diffraction spots, are independent for the three different dimen
sions, while others, such as errors due to uncertainties in camera dimen
sions, film shrinkage, &c., are likely to affect all three cell-dimension
in the same sense. Where there is no evidence to the contrary, it wil
usually be desirable to assume that the errors in the unit-cell dimensions
are not independent, and to use formula ia, since it is better, as a rule
to over-assess the probable error than to under-assess it.

[1] It may be of interest to consider shortly the addition of errors. Where error
are not independent, we can usually say definitely that a positive error in one factor
say δa, will be associated with a positive error in another, δb, and a negative error i
a third, δc, and so on; and the total error is clearly obtained by simple addition wit
due regard to sign, $(\delta a+\delta b-\delta c....)$. But when the errors are independent, we do no
know how their signs are to be associated—a positive error δa may be associate
with a positive δb, or equally likely with a negative δb. If two positive or two nega
tive errors are associated, the total error will be

$$\pm(\delta a+\delta b)=\pm\sqrt{\{(\delta a)^2+(\delta b)^2+2\delta a.\delta b\}};$$

but if one is positive and the other negative, the total will be

$$\pm(\delta a-\delta b)=\pm\sqrt{\{(\delta a)^2+(\delta b)^2-2\delta a.\delta b\}}.$$

Since we do not know the distribution of signs, our best estimate of the probabl
error will be somewhere between these values, and it can be shown that the bes
estimate will in fact be $\pm\sqrt{\{(\delta a)^2+(\delta b)^2\}}$.

Knowing the weight of the unit cell, W, the empirical unit-cell contents are readily calculated from the chemical analysis. For if there is P % of an oxide X_mO_n of molecular weight M, the weight of X_mO_n in the unit-cell must be $PW/100$ and since the weight of a molecule of X_mO_n is $1{\cdot}6603M \times 10^{-24}$ gm., and W will be in units of 10^{-24} gm. if a, b, and c are in Å., the number of molecules of X_mO_n in the unit cell must be $PW/166{\cdot}03M$, and the number of atoms of X in the unit cell is $PWm/166{\cdot}03M$, associated with $PWn/166{\cdot}03M$ atoms of oxygen. The calculations are simplified and shortened by the use of a conversion factor $F = W/1{\cdot}6603S$, where S is the net summation of the analysis after deduction of impurities; by incorporating S in the conversion factor instead of 100, the formal step of recalculating the analysis to 100 % after deduction of impurities is avoided; and F will be subject to a relative error, $\delta W/W$, due to errors in the physical data, together with an error due to errors in the estimation of impurities; the latter error affects S, and if it amounts to δi % it will give rise to a relative error of $\delta i/S$. The total relative error in F, $\delta F/F$, is therefore given by $(\delta F/F)^2 = (\delta W/W)^2 + (\delta i/S)^2$.

The calculations are conveniently set out as in table I, with columns for: the percentages, P; the atomic ratios, Pm/M; the empirical unit-cell contents, $E = FPm/M$; the errors in the empirical unit-cell contents consequent on the errors in the physical data, and in the estimation of impurities, $\delta E = \delta FPm/M$; and the oxygen atoms associated with each element,[1] En/m. Summing the last column, and subtracting the oxygen equivalent of any anions such as Cl′, F′, or S″ in the usual way, we obtain the empirical oxygen content of the unit cell, E_0; this will be subject to an error[2] $\delta_p E_0 = E_0 \delta F/F$ deriving from errors in the physical data and in the estimation of impurities.

It should be noticed that the several errors $\delta_p E$ are not independent, but will all be in the same direction since all depend on δW and on δi. Accordingly, the errors from this source in any group of elements believed to be replacing one another must be simply added, or derived by multiplying the sum of the elements in question by $\delta F/F$.

So far, the only allowance made for errors in the chemical analysis has been the inclusion of δi, the assessed error in the estimation of impurities, in the calculation of the probable error δF of the conversion

[1] A slightly different arrangement is, of course, necessary with minerals such as halides, sulphides, &c.

[2] Here and subsequently, the symbol δ_p is used for an error arising from the errors in the physical data; for errors arising from the chemical analysis alone the symbol δ_c is used, and for the total error from both sources, δ.

factor F. Before considering the effects of analytical errors on the empirical unit-cell contents it will be desirable to consider how the analytical errors (including the error δi in the estimation of impurities) may be assessed. This is, in fact, a matter of the greatest difficulty,

TABLE I. An analysis of nigerite (Min. Mag., 1947, vol. 28, p. 131) recalculated to empirical unit-cell contents, E, together with the errors, $\delta_p E$, in the several elements consequent on errors in the physical data and in the estimation of impurities.

	P %.	Pm/M.	$E = FPm/M$.	$\delta_p E = \delta FPm/M$.	En/m.	Sums.		Partial errors of sums $\delta_p \Sigma$.
TiO_2	0·17	Ti 0·0021	0·02	0·000	0·04	Σ(Sn,Ti)	1·81	0·02
SnO_2	25·33	Sn 0·1681	1·79	0·022	3·58	Σ(Al,Fe‴,Mg)	12·62	0·15
Al_2O_3	50·91	Al 0·9989	10·69	0·130	16·04	Σ(Zn,Fe″,Mn,Pb)	1·04	0·01
Fe_2O_3	11·90	Fe‴ 0·1490	1·59	0·019	2·38	Σ(metals)	15·47	0·19
FeO	2·65	Fe″ 0·0369	0·39	0·005	0·39	Σ(O,OH)	24·35	0·29
ZnO	4·51	Zn 0·0554	0·59	0·007	0·59			
MgO	1·28	Mg 0·0317	0·34	0·004	0·34			
MnO	0·09	Mn 0·0013	0·01	0·000	0·01			
PbO	0·94	Pb 0·0042	0·05	0·001	0·05			
H_2O	1·57	OH 0·1743	1·86	0·023	0·93			
S	99·35			E_n	23·42	(excl. O of H_2O)		
SiO_2	0·48±0·10 = δi			δE_0 =	0·28			
	99·83							

a 5·71±0·02 Å. $\delta a/a$ 0·0035
c 13·86±0·04 Å. $\delta c/c$ 0·0029
$D_{corr.}$ 4·51±0·03 $\delta D/D$ 0·0066

$(\delta W/W)^2 = (2\delta a/a + \delta c/c)^2 + (\delta D/D)^2$
$= (9·9^2 + 6·6^2) \times 10^{-6} = 142 \times 10^{-6}$
$(\delta F/F)^2 = (\delta W/W)^2 + (\delta i/S)^2$
$= 142 \times 10^{-6} + (0·001)^2 = 143 \times 10^{-6}$

$W = a^2cD \sin 60° = 1765·0 \times 10^{-24}$ gm.
$F = W/1·6603S = 10·70$
$\delta F/F = 0·012$
$\delta F = 0·13$

since even a long series of repeat analyses showing excellent agreement may well be affected by a systematic error; this is less likely when analyses have been made by two or more radically different methods, a procedure greatly preferable to simple duplication.

A quantity of data has been amassed for a few types of material;[1] this provides a useful guide to the probable accuracy of an analysis of similar material, but caution is necessary in any attempt to extend these results to other types of material, and where special methods have to be adopted the analyst may have hardly anything to go on unless he carries out test analyses on synthetic samples.

Where an adequate number of test analyses have been made on synthetic samples with a composition reasonably near that of the mineral being studied, it is a simple matter to compute the standard

[1] Hillebrand-Lundell, Applied inorganic analysis. New York and London, 1929, pp. 874–887, 2nd edn. 1953, pp. 3–6; compare W. G. Schlecht, Anal. Chem., 1951, vol. 23, p. 1568; H. W. Fairbairn et al., Bull. U.S. Geol. Survey no. 980, 1951; H. W. Fairbairn and J. F. Schairer, Amer. Min., 1952, vol. 37, p. 744; A. W. Groves, Silicate analysis, 2nd edn., London, 1951, pp. 224–236.

deviation for each constituent; and it may then be assumed with reasonable certainty that the analytical data for the mineral will not be farther from the truth than twice the standard deviation of the test analyses. Properly made up synthetic samples have the advantage of showing up systematic errors in the analytical methods, and where a knowledge of the probable errors of the analysis is of importance, a set of test analyses of such samples is the only really satisfactory check.

For most analyses, however, no such check is available, indeed there is often no other check than a duplicate determination of some or all of the constituents. Sometimes it may be possible to derive a check from the balance of anions and cations in an ionic mineral, or from considerations of the known crystal structure, but this type of check is outside the scope of the present discussion, which is concerned with the information that can be derived from the chemical analysis and physical data alone. Accordingly, in the absence of any direct evidence, the best possible estimate must be made of the probable accuracy of the chemical analysis, and it will be desirable to allow generous possible errors for every constituent. It must be remembered that in the case of constituents that have been determined by difference all the errors in the other constituents concerned fall on the one found by difference; thus in the case of Fe_2O_3, usually determined by difference between the total iron and the ferrous iron, if the error in total iron (as Fe_2O_3) is assessed at t %, and the error in the ferrous iron (as Fe_2O_3) at f %, the error in the ferric iron will be $\sqrt{(t^2+f^2)}$ %; but it should also be remembered that in such a case the variance of the sum of those elements initially weighed together is less than the sum of the variances of the several constituents into which the complex precipitate is ultimately resolved —thus the error in the total iron is t %, and not $\sqrt{\{f^2+(f^2+t^2)\}}$. The special considerations in the case of elements determined by difference will become apparent in the discussion of particular examples, below.

Having assessed the possible errors, δP %, in the several constituents of a mineral whose analysis is reported in terms of oxides, it is a simple matter to calculate the consequent errors in the empirical unit-cell contents, $\delta_c E$, for each element other than oxygen, for as $E = FmP/M$, $\delta_c E = Fm\delta P/M$ (table II). And the total probable error in each element is then obtained by adding the squares of the probable errors derived from the physical and the chemical data, and taking the square root of the sum: $\delta E = \sqrt{\{(\delta_p E)^2+(\delta_c E)^2\}}$. As only two or three significant places need usually be considered, these calculations are quickly performed. The total error in any group of elements in which we are

interested, such as a group believed to replace one another isomorphously, must be found by summation of squares, or by simple summation, or partly by one and partly by the other according as the data are or are not independent. Thus in the example under consideration (tables I and II) the errors in $\Sigma(Al+Fe'''+Mg)$ derived from the physical data are not independent, but those derived from the chemical data are (the Al_2O_3 was determined directly, and not by difference from a mixed precipitate of $Al_2O_3+Fe_2O_3$); accordingly,

$$\{\delta(Al+Fe'''+Mg)\}^2 = (\delta_p\,Al+\delta_p\,Fe'''+\delta_p\,Mg)^2+(\delta_c\,Al)^2+(\delta_c\,Fe''')^2+(\delta_c\,Mg)^2.$$

TABLE II. The errors $\delta_c E$, in the empirical unit-cell contents derived from an analysis of nigerite consequent on the assessed possible errors, δP, in the chemical analysis, together with the total errors, δE, due to both physical ($\delta_p E$, table I) and chemical sources of error.

	δP %.		$\delta Pm/M$.	$\delta_c E = F\delta Pm/M$.	$(\delta_c E)^2 \times 10^4$.	$(\delta_p E)^2 \times 10^4$.	$(\delta E)^2 \times 10^4$.	δE.
TiO_2	0·04	Ti	0·0005	0·005	0·25	0	0·25	0·005
SnO_2	0·30	Sn	0·0020	0·021	4·4	4·8	9·2	0·030
Al_2O_3	0·30	Al	0·0060	0·064	41	169	210	0·145
Fe_2O_3	0·40	Fe'''	0·0050	0·054	29	3·6	32·6	0·057
FeO	0·30	Fe''	0·0040	0·043	18·5	0·25	18·8	0·043
ZnO	0·15	Zn	0·0018	0·019	3·6	0·5	4·1	0·020
MgO	0·10	Mg	0·0025	0·027	7·3	0·2	7·5	0·027
MnO	0·02	Mn	0·0003	0·003	0·1	0	0·1	0·003
PbO	0·10	Pb	0·0005	0·005	0·25	0	0·25	0·005
H_2O	0·20	OH	0·0222	0·238	566	5·3	571	0·239
Total iron (as Fe_2O_3)	0·25	Total Fe	0·0031	0·033	10·9	5·6	16·5	0·041

$\delta\Sigma(Sn,Ti) = \sqrt{\{(0·022)^2+(0·25+4·4)\times10^{-4}\}} = 0·031$
$\delta\Sigma(Al,Fe''',Mg) = \sqrt{\{(0·153)^2+(41+29+7·3)\times10^{-4}\}} = 0·176$
$\delta\Sigma(Zn,Fe'',Mn,Pb) = \sqrt{\{(0·013)^2+(3·6+18·5+0·1+0·25)\times10^{-4}\}} = 0·049$
$\delta\Sigma(metals) = \sqrt{(0·19)^2+(0·25+4·4+41+3·6+7·3+0·1+0·25+10·9)\times10^{-4}\}} = 0·207$

But in deriving the error in the total metal atoms per unit cell,[1] $\delta\Sigma$(metals), we must add in $(\delta_c\,Fe_{total})^2$, and not $(\delta_c\,Fe'')^2+(\delta_c\,Fe''')^2$, since Fe_2O_3 is determined by difference between total iron and ferrous iron, and the total iron is involved in Σ(metals). In general, due consideration should be given to the actual analytical methods employed in their bearing, not only on the individual errors of the several elements, but on the errors of any groups of elements in which we may be interested.

[1] Strictly speaking, the errors added in finding Σ(metals) will not all be truly independent, since the total error in all the oxides is necessarily $(100-S\pm\delta i)$; and δi has already been incorporated in δF.

We have now assessed the probable errors in each element present in the mineral, except oxygen. The most obvious course would be to simply calculate the errors in the oxygen content, $Fn\delta P/M$, for each oxide reported in the analysis, and add them through their squares, as independent errors. But a simple consideration will show that this course is likely to lead to a considerable exaggeration of the error in the oxygen atoms per unit cell consequent on errors in the chemical analysis. For if we consider a mineral in which all the constituent oxides contain the same percentage of oxygen (as, for example, MgO and TiO_2 do approximately), no error of analysis, however gross, will affect the percentage of oxygen found for the mineral and, therefore, the number of oxygen atoms per unit cell found.

Errors of chemical analysis can take two forms—errors of determination and errors of separation, the former being independent for all the oxides present, while the latter are not since an underestimate of one oxide is necessarily coupled with an overestimate of another. In some minerals, particularly when the number of elements present is very small, it may be desirable to take special consideration of the errors of separation, and such a case will be considered below, but in general it will suffice to assume that the analytical errors and their effects on the oxygen figure are independent,[1] and to regard them all as errors of determination that chance to balance out more or less completely.

Regarding the analytical errors, then, as independent errors of determination, each will affect the observed percentage of oxygen in the mineral in proportion to the difference between the percentage of oxygen n the mineral and that in the oxide. The percentage of oxygen in the mineral can readily be calculated by the general relation $E = FP/M$ from the number of oxygen atoms per unit cell, E_0, which has already been found (table I); from this, the oxygen percentage in the mineral, $P_0 = 16E_0/F$. We now take the differences, Δ, between the percentage oxygen in the mineral, P_0, and the percentages in the several oxides[2] (col. Δ, table III); then the error δP in the analytical determination of each oxide will involve an error in the number of oxygen atoms $\delta_c E_0 = F\Delta\delta P/1600$. These errors are squared and summed, the square root of the sum giving the probable total error in the oxygen content due to analytical errors (table III), to which must be added the error

[1] The assumption that the errors of separation are independent is only likely to be serious when two of the oxides concerned in any particular separation, wrongly taken as independent, differ widely in oxygen percentage—e.g. Yt_2O_3 and Ce_2O_3.

[2] The percentages of oxygen in the principal mineral-forming oxides are listed in table V.

TABLE III. Calculation of the probable error in the oxygen content of the unit cell consequent on the assessed probable errors in the chemical analysis of nigerite, and of the total error in the oxygen due to both physical (table I) and chemical sources of error. For details see text.

	O % = $1600n/M$.	Δ.	$F\Delta/1600 \times 10^2$.	δP.	$\delta_c E_0 = F\Delta\delta P/1600 \times 10^2$.	$(\delta_c E_0)^2 \times 10^4$.
TiO_2	40·05	5·03	3·36	0·04	0·13	0·02
SnO_2	21·23	−13·79	−9·22	0·30	−2·77	7·67
Al_2O_3	47·09	12·07	8·07	0·30	2·42	5·86
Fe_2O_3	30·76	−4·26	−2·85	0·25	−0·71	0·50
ZnO	19·66	−15·36	−10·27	0·15	−1·54	2·37
MgO	39·70	4·68	3·13	0·10	0·31	0·10
MnO	22·56	−12·46	−8·33	0·02	−0·17	0·03
PbO	7·17	−27·85	−18·62	0·10	−1·86	3·46
H_2O	88·81	53·79	35·97	0·20	7·19	51·70
					$\Sigma(F\Delta\delta P/1600)^2$	$71·71 \times 10^{-4}$
					Σ, excl. H_2O	$20·01 \times 10^{-4}$

% Oxygen in nigerite = $16E_0/F$ = 35·02 %.
Error in O due to the FeO determination (δP = 0·30 %) = $F\delta P/2M$ = 0·022.
Error in Σ(O, OH) due to other analytical errors = $\sqrt{\{\Sigma(F\Delta\delta P/1600)^2\}}$ = 0·085.
Error in O due to other analytical errors = 0·045.
Error in O due to physical sources (table I) = 0·29.
Total error in Σ(O,OH) = $\sqrt{\{(0·085)^2+(0·022)^2+(0·29)^2\}}$ = 0·30.
Total error in O = $\sqrt{\{(0·045)^2+(0·022)^2+(0·29)^2\}}$ = 0·295.

TABLE IV. The empirical unit-cell contents of nigerite, with their probable errors, based on the assessed errors of the chemical analysis and physical data (from tables I–III).

TiO_2	0·17±0·04	Ti	0·02±0·01	Σ(Sn,Ti)	1·81±0·03
SnO_2	25·33±0·30	Sn	1·79±0·03	Σ(Al,Fe‴,Mg)	12·62±0·18
Al_2O_3	50·91±0·30	Al	10·69±0·15	Σ(Zn,Fe″,Mn,Pb)	1·04±0·05
Fe_2O_3	11·90±0·40	Fe‴	1·59±0·06	Σ(metals)	15·47±0·21
FeO	2·65±0·30	Fe″	0·39±0·04		
ZnO	4·51±0·15	Zn	0·59±0·02	Σ(O,OH)	24·35±0·30
MgO	1·28±0·10	Mg	0·34±0·03		
MnO	0·09±0·02	Mn	0·01±0·00		
PbO	0·94±0·10	Pb	0·05±0·01		
H_2O	1·46±0·20	OH	1·86±0·24		
S	99·35	O	22·49±0·29		
SiO_2	0·48±0·10				
	99·83				

Total iron as Fe_2O_3 14·84±0·25

a 5·71±0·02 Å.
c 13·86±0·04 Å.
D 4·51±0·03

The approximation of Σ(O,OH) to the integral 24 is clearly within the limits of probable error, but Σ(metals) probably departs significantly from either of the integral values 16 or 15.

due to errors in the physical data. In making this summation, it must be remembered that the quantities directly determined are not the percentages of Fe_2O_3 and FeO, but the total iron (as Fe_2O_3) and the net state of oxidation of the mineral, which in an under-oxidized mineral is normally reported as FeO. Accordingly, the entries in table III are for total iron as Fe_2O_3, not for Fe_2O_3 and FeO, and a separate calculation is made of the effect of error in the ferrous oxide determination on the oxygen content; the latter will clearly be $F\delta P/2M$, or $\frac{1}{2}\delta_c E_{Fe''}$, and is an independent error to be added to the others. The final results of these calculations are summarized in table IV.

TABLE V. Percentages of oxygen in the principal mineral-forming oxides.

H_2O	88·81	NiO	21·42	As_2O_3	24·26	UO_2	11·85
Li_2O	53·55	CuO	20·12	Sb_2O_3	16·47	N_2O_5	74·07
Na_2O	25·81	ZnO	19·66	Bi_2O_3	10·30	P_2O_5	55·64
K_2O	16·99	PbO	7·17	CO_2	72·71	As_2O_5	34·81
Cu_2O	11·18	B_2O_3	68·92	SiO_2	53·28	Sb_2O_5	24·73
BeO	63·97	Al_2O_3	47·09	GeO_2	30·59	Nb_2O_5	30·10
MgO	39·68	Cr_2O_3	31·58	SnO_2	21·23	Ta_2O_5	18·11
CaO	28·53	Mn_2O_3	30·41	TiO_2	40·05	SO_3	59·55
SrO	15·44	Fe_2O_3	30·06	ZrO_2	25·97	CrO_3	49·00
BaO	10·43	Yt_2O_3	21·25	HfO_2	15·20	MoO_3	33·34
MnO	22·56	La_2O_3	14·73	ThO_2	12·12	WO_3	20·70
FeO	22·27	Ce_2O_3	14·62	MnO_2	36·81	UO_3	16·78
CoO	21·35	Lu_2O_3	12·06	CeO_2	18·59		

Considering the results of these calculations as applied to the analysis of nigerite, we note that: the total error in the oxygen content from chemical sources is comparable with that in any other major constituent element such as Al; despite a fairly generous assessment of the probable error of the chemical analysis, the physical data remain the main source of error in the cell-contents as far as the major constituents and their sums are concerned; and the analysis appears to afford substantial evidence that there are vacancies in one or other of the sets of lattice positions occupied by metal ions, since $\Sigma(\text{metals}) = 15{\cdot}47 \pm 0{\cdot}21$, while the oxygen positions are probably completely occupied, since $\Sigma(\text{O,OH}) = 24{\cdot}35 \pm 0{\cdot}30$.

It should be added that the limits of error calculated in this way from the assessed errors of a single analysis and set of physical data have no statistical significance, and are mere estimates (it is for that reason that they have been referred to as 'probable errors' and not variances); too much weight should not be attached to the actual figures found. On the other hand, when taken in conjunction with a considerable number of similar calculations made on minerals for which both chemical

and X-ray data have been obtained, there is clear evidence that th errors in empirical unit-cell contents are not usually so great as som recent studies of rock and mineral analyses might suggest, and in parti cular that analytical error will rarely affect the observed oxygen atom per unit cell seriously. Thus in the case of the nigerite analysis dis cussed above, $24{\cdot}35 \pm 0{\cdot}30$ may be taken as a reasonable approach t $24{\cdot}00$; but on the other hand, $15{\cdot}47 \pm 0{\cdot}21$ is probably a truly significan departure from 16·00. In general, we may say that if we can assum a certain probability that the true value is within the assigned range there is something like ten times that probability that it is within twic the assigned range.

TABLE VI. Empirical unit-cell contents for matlockite (Min. Mag., 1934, vol. 23 p. 589).

	P %.	δP.	P/M.	$\delta P/M$.	$E = FP/M$.	$\delta_p E = \delta FP/M$.	$\delta_c E = F\delta P/M$.	$(\delta_p E)^2 \times 10^4$.	$(\delta_c E)^2 \times 10^4$.	$(\delta E)^2 \times 10^4$.	δE.
Pb	$79{\cdot}55 \pm 0{\cdot}5$		0·3839	0·0024	1·979	0·0315	0·0124	9·9	1·5	11·4	0·0344
F	$7{\cdot}11 \pm 0{\cdot}5$		0·3742	0·0263	1·929	0·0307	0·135	9·4	182	191	0·1388
Cl	$13{\cdot}44 \pm 0{\cdot}1$		0·3791	0·0028	1·954	0·0311	0·0144	9·7	2·1	11·8	0·0344
	100·10								$\Sigma \delta E_{(F,Cl)}$	203	0·1423

D	$7{\cdot}05 \pm 0{\cdot}07$	$\delta D/D$	0·010
a	$4{\cdot}10 \pm 0{\cdot}02$ Å.	$\delta a/a$	0·005
c	$7{\cdot}23 \pm 0{\cdot}02$ Å.	$\delta c/c$	0·003

$(\delta F/F)^2 = (\delta W/W)^2$
$= (2\delta a/a + \delta c/c)^2 + (\delta D/D)^2$
$= (10+3)^2 \times 10^{-6} + 100 \times 10^{-6} = 269 \times 10^{-6}$

$W = a^2cD = 856{\cdot}8 \times 10^{-24}$ g. $\quad \delta F/F = 0{\cdot}016$

$F = W/1{\cdot}6603\,S = 5{\cdot}155$ $\quad \delta F = 0{\cdot}082$

Pb	$1{\cdot}98 \pm 0{\cdot}03$	+ valencies = $2\text{Pb} = 3{\cdot}96 \pm 0{\cdot}06$
F	$1{\cdot}93 \pm 0{\cdot}14$	− valencies = $\Sigma(\text{F}+\text{Cl}) = 3{\cdot}88 \pm 0{\cdot}14$
Cl	$1{\cdot}95 \pm 0{\cdot}03$	

The low value for both + and − valencies suggests that either one of the cell-sides or the density is a little too low. Since there are only three constituent elements, any positive error in one constituent must have been compensated by a negative error in another; but the column $\delta_c E$ shows that (owing to the great difference in their atomic weights) a 0·5 % increase in F would increase the F atoms per unit cell by 0·13 % while a balancing 0·5 % decrease in Pb would only reduce the Pb atoms per unit cell by 0·01 %. It is clear that the experimental data agree with an ideal of 2PbFCl per unit cell within their assessed probable error.

A number of further examples have been worked out to illustrate the method. In table VI calculations have been made for a particularly simple analysis, matlockite. Table VII illustrates the procedure when the constituent believed to be most liable to error (here B_2O_3) has an oxygen percentage markedly different from that of the mineral as a whole; a positive error in the percentage of B_2O_3, with more oxygen than the mineral as a whole, will entail a positive error in the observed oxygen atoms per unit cell, and will necessarily be accompanied by negative errors in some of the other constituents since the summation is

nearly 100 %: but the other constituents have oxygen percentages less than that of the mineral as a whole and so their negative percentage errors entail a positive error in the oxygen atoms per unit cell; therefore in this case we add the $\delta_c E_0$ values themselves, and not their squares as we should if the errors were fully independent.

TABLE VII. Empirical unit-cell contents for sinhalite (Min. Mag., 1952, vol. 29, p. 848). Here it is found more appropriate to add the partial errors in the oxygen content due to errors in the chemical analysis directly rather than through their squares, for reasons given in the text.

	P %.	δP.	$\frac{Pm}{M}$.	$\frac{\delta Pm}{M}$		$\frac{E=FPm}{M}$.	$\frac{En}{m}$.	$\frac{\delta_p E=F\delta Pm}{M}$.	$\frac{\delta_c E=P\delta Fm}{M}$.	δE	$\frac{\%\ O=1600n}{M}$.	Δ.	$\frac{\delta_c E_0=F\Delta\delta P}{1600}$.
B_2O_3	24·2±1·5		0·6950	0·0430	B	3·55	5·32	0·220	0·015	0·22	68·93	19·52	0·096
Al_2O_3	41·0±0·5		0·8044	0·0098	Al	4·10	6·15	0·050	0·017	0·05	47·09	− 2·32	0·004
Fe_2O_3	2·0±0·2		0·0250	0·0025	Fe'''	0·13	0·20	0·013	0·000	0·01	30·76	−18·65	0·012
MgO	32·3±0·5		0·8014	0·0124	Mg	4·09	4·09	0·063	0·017	0·07	39·70	− 9·71	0·016
S	99·5					E_0	15·76						$\Sigma\delta_c E_0$ 0·128
H_2O	0·3±0·3 = δi												
	99·8												

% oxygen in sinhalite $= 16E_0/F = 49{\cdot}41$

$\delta E = \sqrt{\{(\delta_p E)^2 + (\delta_c E)^2\}}$

$\delta\Sigma(\mathrm{Mg,Fe,Al,B}) = \sqrt{\{\Sigma(\delta E)^2\}} = 0{\cdot}24$

D	3·475±0·005	$\delta D/D$	0·0015	$(\delta W/W)^2 = (\delta a/a+\delta b/b+\delta c/c)^2+(\delta D/D)^2$
a	4·328±0·005 Å.	$\delta a/a$	0·0012	$= 0{\cdot}0026^2+0{\cdot}0015^2$
b	9·878±0·005 Å.	$\delta b/b$	0·0005	$\delta W/W = 0{\cdot}0030$
c	5·675±0·005 Å.	$\delta c/c$	0·0009	$(\delta F/F)^2 = (\delta W/W)^2+(\delta i/S)^2$
				$= 0{\cdot}0030^2+0{\cdot}0030^2$

$W = abcD = 843{\cdot}1\times10^{-24}$ gm. $\qquad \delta F/F = 0{\cdot}0042$

$F = W/1{\cdot}6603S = 5{\cdot}103$ $\qquad \delta F = 0{\cdot}021$

	B	3·55±0·22
$\delta_p E_0 = E_0\delta F/F = 0{\cdot}066$	Al	4·10±0·05
	Fe'''	0·13±0·01
$\delta E_0 = \sqrt{\{(\delta_p E_0)^2+(\delta_c E_0)^2\}}$	Mg	4·09±0·07
$= \sqrt{\{(0{\cdot}066)^2+(0{\cdot}128)^2\}}$	O	15·76±0·14
$= 0{\cdot}144$	Σ(Mg,Al,Fe,B)	11·87±0·24

The empirical unit cell contents clearly indicate some substitution of (Al,Mg) for B; they also suggest that the sum (Mg + Al + Fe + B) is integral and that there are some vacancies in the oxygen lattice, but the evidence is not conclusive in this respect.

Doubts concerning the function of water in a mineral, or its true amount, are probably the commonest cause of uncertainty in the unit-cell contents. Water is tenaciously adsorbed by many minerals, especially in fine powder, so that it is often very difficult to decide whether small amounts of water found on analysis are constitutional or impurities. The problem is all the more troublesome because water contains a higher percentage of oxygen (89 %) than any other oxide, so that uncertainties in the water content have a particularly serious effect on the oxygen atoms per unit cell, because water has a particularly low molecular weight, and because its accurate determination is often unexpectedly difficult. Accordingly, it is often desirable not only to assign

an ample probable error to the water determination, but to make spe[illegible] calculations of the effect on the unit-cell contents of a mistake in t[illegible] allocation of the water found to constitutional or adsorbed water.

If the mineral contains h % of water which was either not determi[illegible] or was accounted an impurity (adsorbed or included water), the n[illegible] sum, S, will be low by h %: the observed density will be correct if t[illegible] presence of the water was not recognized, but if it was regarded as a[illegible] impurity and a density correction made, this correction will have to [illegible] subtracted from the 'corrected' density. The first factor will redu[illegible] the conversion factor F by $Fh/(S+h)$, while the latter will also red[illegible] F, by $Fh(D-1)/\{100D+h(D-1)\}$, where S is the net sum excluding [illegible] water, and D the 'corrected' density. Thus the corrected value o[illegible] will be:

$$F-\Delta F = F-\frac{Fh}{S+h}$$

if the density D had not been 'corrected' for the supposedly adsorb[illegible] water, but

$$F-\Delta F=F-\frac{FhD}{100}$$

if the correction had been made.[1] All the unit-cell contents except th[illegible] oxygen will now be reduced by $\Delta FPm/M$: the corrected total oxyge[illegible] will be:

$$\Sigma(\mathrm{O,OH}) = E_0-E_0\Delta F/F+Fh/18.$$

If the water is to be reported as hydroxyl, it will amount to $hF/9$ aton[illegible] per unit cell. The water determination will, of course, have been subjec[illegible] to an error, say δh %, and this must be taken account of in the usua[illegible] way; it will often be an appreciable fraction of h, and will affect th[illegible] corrections in all the other elements present, through F; as these error[illegible] will all be in the same direction, it will be appropriate to incorporat[illegible] the error with the errors in F arising from uncertainties in the physic[illegible] data.

In table VIII the empirical unit-cell contents have been calculate[illegible]

[1] More exactly

$$F-\Delta F = F\left(1-\frac{h}{S+h}\right)\left(1-\frac{h(D-1)}{100+h(D-1)}\right);$$

if h is less than about 5% and $S+h$ does not depart seriously from 100%, the simple expression is adequate. It is perhaps appropriate to mention here that the densit[illegible] correction for x% of an impurity of density d is

$$D_c-D_0 = xD_0(D_0-d)/(100\,d-xD_0),$$

where D_c is the corrected and D_0 the observed.

from an analysis of kornerupine (J. P. Girault, Amer. Min., 1952, vol. 37, p. 535, analysis 5b [M.A. 12 227]), assuming the water is an impurity, and also assuming the water is present as hydroxyl groups, using the above procedure to make the appropriate corrections. A comparison with Girault's table 5 raises several interesting points. The two tables agree fairly well when the water is assumed to be an essential constituent (table VIII, col. E^{+}; Girault's table 5, col. 6), but there are small differences, especially in the oxygen atoms per unit cell; these arise from three sources: the values of a, b, and c in table VIII have been calculated from the original measurements, which are in kX, by use of the factor 1·0022 and then rounded off to 0·01, but if the original kX values are used with the appropriate factor for the weight of a hydrogen atom, we find a value for F^{+} 0·02 greater; then the value of ΔF has been calculated in table VIII from the rounded off figure for the density as 'corrected' for 0·97 % H_2O, but if F^{+} is calculated direct using the observed density of 3·37, we find a value another 0·03 greater; that is, the values of F^{+}, and therefore of E^{+} in table VIII, are 0·15 % low (F^{+} should be 29·81), which will increase the discrepancies as compared with Girault's table 5. With these corrections, the difference between the values of E^{+} in table VIII and col. 6 of Girault's table 5 amounts to 0·7 %, suggesting that Girault has used the wrong value for the weight of a hydrogen atom (1·6603 if Å. are in use, but 1·649 if kX are used, a difference of 0·7 %).

Turning to the unit-cell contents counting the water as an impurity (table VIII, col. E^{-}; Girault's table 5, col. 2), Girault's figure of 24·3 for Al is an arithmetical slip for 24·0, and involves a reduction in the oxygen content to 85·6. The figures in table VIII are again 0·06 % low owing to the conversion of the original kX units to Å. and rounding off of the results, and Girault's figures are 0·7 % low owing to the use of 1·6603 instead of 1·649 in the calculation of F, but there remains a discrepancy of about 1·7 %. This is probably due to the use by Girault of the measured density of 3·37 in calculating the unit-cell contents with water taken as an impurity, which would make his results 2·3 % low; if the water is an impurity, the density must be corrected for it.

Finally, it will be clear from the values of δE in table VIII that no conclusion can be drawn concerning the role of the water in kornerupine unless much more accurate data can be obtained. To bring δE_0 down to 0·4, which is probably the maximum value that would allow of safe deductions, the chemical analysis, cell-dimensions, and density would all have to be more accurate; if the relative error in the cell-dimensions

TABLE VIII. An analysis of kornerupine (Amer. Min., 1952, vol. 37, p. 535), interpreted assuming the water is an impurity (E^-) and also assuming it is an essential constituent (E^+).

	P %.	δP.		Pm/M.	$\delta Pm/M$.	$\delta_p E$.	$\delta_c E$.	O %.	Δ.	$\delta_c E_0$.	$E^- n/m$.	$E^+ n/m$.		E^-.	E^+.	δE.
SiO_2	30·32	±0·30	Si	0·5047	0·005	0·15	0·15	53·26	7·38	0·042	31·08	30·04	Si	15·54	15·02	±0·21
B_2O_3	3·51	±0·20	B	0·1008	0·003	0·03	0·18	68·93	23·05	0·088	4·65	4·50	B	3·10	3·00	±0·18
Al_2O_3	40·97	±0·30	Al	0·8038	0·006	0·24	0·15	47·09	1·21	0·007	37·12	35·88	Al	24·75	23·92	±0·28
Fe_2O_3	0·42	±0·40	Fe‴	0·0053	0·005	0·00	0·15	30·76	−15·12	0·058	0·24	0·24	Fe‴	0·16	0·16	±0·15
FeO	8·52	±0·30	Fe″	0·1186	0·004	0·04	0·12	—	—	—	3·65	3·58	Fe″	3·65	3·58	±0·13
MgO	14·91	±0·10	Mg	0·3700	0·0025	0·11	0·08	39·70	−6·18	0·012	11·04	11·02	Mg	11·04	11·02	±0·15
CaO	0·06	±0·03	Ca	0·0053	0·0006	0·00	0·02	28·53	−17·35	0·010	0·03	0·03	Ca	0·03	0·03	±0·02
Na_2O	0·08	±0·05	Na	0·0026	0·002	0·00	0·06	25·81	−20·07	0·009	0·04	0·04	Na	0·08	0·08	±0·06
P_2O_5	0·09	±0·03	P	0·0013	0·0004	0·00	0·01	56·32	10·44	0·006	0·10	0·10	P	0·04	0·04	±0·01
S^-	98·88															
H_2O	0·97	±0·20	OH	0·1077	0·022	0·03	0·66	88·81	42·93	$\sqrt{\{\Sigma(\delta_c E_0)^2\}}$0·13			O	88·31	83·83	±0·89
S^+	99·85											1·60	OH	—	3·20	±0·66
										$\sqrt{\{\Sigma(\delta_c E_{O,OH})^2\}}$0·21			Σ(O,OH)	—	87·03	±0·90
Total iron as Fe_2O_3	9·88	±0·20;	$\delta_p E$(Fe total) = 0·10										Σ(Si,B)	18·64	18·02	±0·30
													ΣR	40·11	38·83	±0·45
													Σ(Al, Fe‴)	24·91	24·08	±0·32
													Σ(Mg, Fe″, Ca, Na, P)	15·20	14·75	±0·22

TABLE VIII (*contd.*)

$D_{corr.}$ 3·45 ± 0·01 (corrected for 0·97 % H_2O taken as impurity)

[D	3·37 ± 0·01]	$\delta D/D$	0·003
		$\delta i/S$	0·002
a	13·72 ± 0·04 Å.	$\delta a/a$	0·003
b	15·97 ± 0·04 Å.	$\delta b/b$	0·003
c	6·69 ± 0·02 Å.	$\delta c/c$	0·003

$$(\delta F/F)^2 = (0{\cdot}009)^2 + (0{\cdot}003)^2 + (0{\cdot}002)^2$$

$F^- = abcD/1{\cdot}6603S$ $\quad \delta F/F = 0{\cdot}010$

$F^- = 30{\cdot}80$ $\quad \delta F = 0{\cdot}30$

$\delta_p E_0 = 88{\cdot}31 \times 0{\cdot}010 = 0{\cdot}88$

$(\delta E_0)^2 = (\delta_p E_0)^2 + \Sigma(\delta_c E_0)^2 + (\frac{1}{2}\delta E_{Fe''})^2$
$= 0{\cdot}76 + 0{\cdot}017 + 0{\cdot}004$

$\delta E_0 = 0{\cdot}89$

$\{\delta\Sigma(O, OH)\}^2 = (\delta_p E_0)^2 + \Sigma(\delta_c E_{(O,OH)})^2 + (\frac{1}{2}\delta E_{Fe''})^2$
$= 0{\cdot}77 + 0{\cdot}044 + 0{\cdot}004$

$\delta\Sigma(O, OH) = 0{\cdot}90$

$(\delta\Sigma R)^2 = (0{\cdot}40)^2 + (0{\cdot}15)^2 + (0{\cdot}10)^2 + (0{\cdot}08)^2 + (0{\cdot}02)^2 + (0{\cdot}06)^2 + (0{\cdot}01)^2$

$\delta\Sigma R = 0{\cdot}45$ (R includes Al, Fe, Mg, Ca, Na, P)

$\Delta F/F = \dfrac{0{\cdot}97 \times 3{\cdot}45}{100}$
$= 0{\cdot}0334$

$\Delta F = 1{\cdot}04$

$F^+ = 29{\cdot}76$

% oxygen in kornerupine $= 88{\cdot}31 \times 16/F$
$= 45{\cdot}88$ %

$\delta_c E_0$ due to error in FeO $= \frac{1}{2}E_{Fe''}$
$= 0{\cdot}06$

$\delta\Sigma(Si,B) \sqrt{\{(0{\cdot}15 + 0{\cdot}03)^2 + (0{\cdot}15)^2 + (0{\cdot}18)^2\}}$
$= 0{\cdot}30$

$\delta\Sigma(Al,Fe''') = \sqrt{\{(0{\cdot}24)^2 + (0{\cdot}15)^2 + (0{\cdot}15)^2\}}$
$= 0{\cdot}32$

$\delta\Sigma(Mg,Fe'',Ca,Na,P) = \sqrt{\{(0{\cdot}15)^2 + (0{\cdot}12)^2 + (0{\cdot}08)^2 + (0{\cdot}02)^2 + (0{\cdot}06)^2 + (0{\cdot}01)^2\}}$
$= 0{\cdot}22$

Since the major error in all the sums arises from δF, the sign of all these errors is likely to be the same.

could be reduced to 0·001, and that in the density to 0·002, a lit[tle] improvement in the analysis, especially in the boron and water det[er]minations, might allow the role of the water to be established.

The above example suggests that we should give some consideratio[n] to the matter of calculating and rounding off the results of quantitati[ve] observations. On the one hand, it is clearly pointless to quote resu[lts] to four or more significant figures when inevitable sources of error ma[y] affect the second significant figure: but on the other hand it is equa[lly] undesirable to add unnecessarily to the errors in calculating the pub[-] lished results from the actual measurements. For example, it is usua[l] in a rock analysis to take about 1 gram of rock powder for the 'ma[in] portion'; this is weighed on a balance that is usually adjusted to wei[gh] to 0·1 mg., and the silica obtained is weighed on the same balance: th[e] four weighings involved, each to $\pm 0{\cdot}1$ mg., involve a total error of th[e] order of $\pm 0{\cdot}02$ in the percentage of silica: accordingly, even if there were no other sources of error, a third decimal place in the silica percen[t]tage could have no significance. But on the other hand, if 1·0045 gram of rock powder yielded 0·5372 gram of silica, the percentage of silica comes to 53·50 % if four-figure logarithms are used in the calculations but 53·48 % if five-figure logarithms are used; clearly four-figure logarithms are not adequate where the measurements run to four significant figures.

An idea that appears to be widely held is that if the actual measure[-] ments are known to be liable to an error in, say, the first decimal place it is justifiable to round them off to that place before working out the results dependent on them, in the expectation that the relative error in the results will be unaffected, while much labour will have been saved. This is not strictly true, and the relative error will commonly be appreci[a]bly increased.

The reason is readily seen from the above example. If the weighing of rock powder, 1·0045 gram, was liable to an error which we estimate at ± 1 mg., or a relative error of 0·001, this implies that we estimate the true weight to fall between 1·0035 and 1·0055 gram: if we round-off the weight to 1·005 gram before calculation of the silica percentage, we must increase the assessed relative error to 0·0015, since our lower limit (1·0035 gram) differs by that much from our rounded-off weight. In fact, calculation with ± 1 mg. in both the weight of rock and that of SiO_2 yields SiO_2 53·50 % $\pm 0{\cdot}13$ % if no rounding-off is carried out, but 53·4 % $\pm 0{\cdot}2$ % if we round-off the weighings before calculation.

Again, it is often held that although rounding-off may affect the result

appreciably when only a few measurements are involved, if the final result involves a large number of measurements the effects of rounding-off will necessarily tend to cancel out. This is a confusion with the well-known fact that independent errors tend to cancel out when compounded, and is quite untrue, as the calculations[1] summarized in table IX show. We assume that n measurements have been made, and that the quantity sought is their sum: each of the measurements will be liable to error, and since the first place of decimals was uncertain, each measurement has been rounded-off to the nearest integer before summation. If now we compare the sums obtained by this method and by adding the measurements without any rounding-off, and then rounding-off the sum, we find that in fact the results are liable to differ, and the probability of a difference increases the greater the number of measurements; with 7 or more measurements, the sum of the rounded-off measurements is as likely to differ from the rounded-off sum of the actual measurements by at least one unit as it is to agree (see table IX).

TABLE IX. A table of the probability that the sum of n measurements each of which has been rounded-off to the nearest integer will differ by ϵ units from the rounded-off sum of the same n measurements summed before rounding-off. The probabilities for negative values of ϵ are, of course, the same as those here tabulated for positive values.

$n\rightarrow$ / $\epsilon\downarrow$	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
0	1	0·75	0·670	0·600	0·550	0·510	0·482	0·456	0·429	0·408	0·390
1		0·125	0·165	0·1975	0·217	0·230	0·236	0·241	0·244	0·246	0·247
2				0·0025	0·008	0·015	0·023	0·031	0·041	0·048	0·055
3						2×10^{-6}	2×10^{-4}	6×10^{-4}	0·0013	0·0024	0·0027
4								5×10^{-8}	2×10^{-6}	1×10^{-5}	4×10^{-5}
5										1×10^{-10}	1×10^{-8}

We conclude that it is generally desirable, since the additional time spent in calculations will never be comparable with the time spent on the analysis, to carry out all calculations to at least one place beyond the first significant figure liable to be affected by known sources of error, and to take care that the mathematical instruments (tables or slide-rules) used are adequate to this task. It will also usually be desirable to attempt some estimate of the accuracy of the several measurements made, and to calculate the effect on the final results of the several assessed errors.

[1] If the frequencies of observations in the ranges $A-0{\cdot}50$ to $A-0{\cdot}40$, $A-0{\cdot}40$ to $A-0{\cdot}30$,..., $A+0{\cdot}40$ to $A+0{\cdot}50$ are all equal, then a random sample of n observations will have a probability p of giving a sum $nA+\Delta/10$, where p is the coefficient of x^{Δ} in the expansion of $G(x)=\left(\dfrac{1+x+x^2\ldots+x^9}{10x^{9/2}}\right)^n$.

Investigation of the crystal structure of antigorite.

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Summary of previous X-ray work.

Selfridge (1936) examined by chemical, optical, and X-ray powder methods a large number of specimens of serpentine mineral (ideal formula $H_4Mg_3Si_2O_9$), many of which were known as antigorite. He found that nearly all gave similar powder photographs, indicating close structural relationship, but that there were noticeable differences on the basis of which the specimens could be separated into two groups, one giving a photograph similar to that of chrysotile asbestos, and the other containing the varieties called antigorite. Gruner (1937) came to similar conclusions, and in addition he indexed most of the reflections using the cell dimensions a 5·33, b 18·5, c $2 \times 7{\cdot}33$ Å., β 93°, remarking in particular on the correspondence between $00l$ reflections in the two groups.

Aruja (1944) reported investigation of an antigorite from Mikonui, New Zealand, this being the first X-ray 'single-crystal' study of a serpentine mineral. He determined the cell dimensions and space group, and noted the close relationship between these data and those of chrysotile (table I). In this case both $00l$ and $0k0$ reflections were seen to be similar to those from chrysotile. The most outstanding feature of the X-ray photographs obtained is that of the large 'a'-axis (table I). Aruja's conclusions were mainly as follows.

That there is in the antigorite structure a sequence of atomic planes parallel to (001) similar to that in chrysotile. Taking the sub-cell 'a' dimension as one-eighth of the large cell value, i.e. 5·44 Å., it was suggested that the resulting axial ratio $b:a = 1:1{\cdot}703$ may indicate a chain structure parallel to 'a' rather than a sheet structure, and that the coarsely fibrous nature parallel to the 'b'-axis observed in many antigorites was due to what Selfridge (1936) had described as a 'false fibre' effect. The large 'a'-axis was interpreted as a superlattice dimension perhaps due to a regularly occurring distortion, or else a polymorphism of the sort exhibited by sheet structures but here involving atomic

chains. Streaks occurring through certain diffraction spots were partly accounted for by assuming some randomness in the sequence of successive cells.

TABLE I. Comparison between cell dimensions of chrysotile and antigorite.

	a.	*b*.	*c*.	*β*.
Chrysotile (Whittaker, 1952)	5·33	9·2	$2\times7{\cdot}33$ Å.	93° 7′
Antigorite (Aruja, 1944)	43·5	9·26	7·28	91 24

MORPHOLOGY AND OPTICS.

The rock specimen[1] from Cross river, Mikonui, New Zealand, and its constituents were described by Bonney (1908), and a description of the antigorite crystals was given by Aruja (1944). Some further observations have now been made.

Two different kinds of antigorite grain occur in the rock. The crystal used for the X-ray analysis was a small rectangular plate with morphology and optics as follows. Length of plate parallel to *b*. '*c*'-axis nearly perpendicular to plate. Cleavage, probably (100), parallel to the '*b*-'axis; occasional (010) and perfect (001) cleavage. Extinction well defined and straight. α 1·560, β 1·563, γ 1·564$\pm$0·001 (Na-light); 2V negative 55$\pm$2°; dispersion weak, $r > v$; $\gamma = b$, α and β nearly parallel to *c* and *a* respectively.

There are also present, in roughly equal quantity, grains which have a mottled appearance between crossed nicols, and have small inclusions of a magnetic iron-ore. The mean refractive index of such grains is 1·563$\pm$0·002. The two types of grain were separated magnetically and the X-ray powder photographs of the two fractions were seen to be almost identical. It is assumed, therefore, that the difference between them is one of texture only. (The iron-ore mineral is present in such small quantity that it does not give observable lines on a moderately exposed powder photograph.)

The optical properties listed above are similar to those reported by Selfridge (1936) for several varieties of antigorite, but in the latter cases where 2V was observed it was found to be small. Similar values are given also by Hess, Smith, and Dengo (1952), α 1·5615, β 1·5660, γ 1·5670$\pm$0·0005, 2V 47½$\pm$½°, but the crystallographic axes were not explicitly determined. If what is there described as a (100) parting is in fact (010) then the optical scheme is the same as that described

[1] The specimen (no. 11566) was kindly supplied from the Department of Mineralogy and Petrology, Cambridge University.

above. If it is truly (100) then the β and γ directions are reversed wi respect to the 'a'- and 'b'-axes.

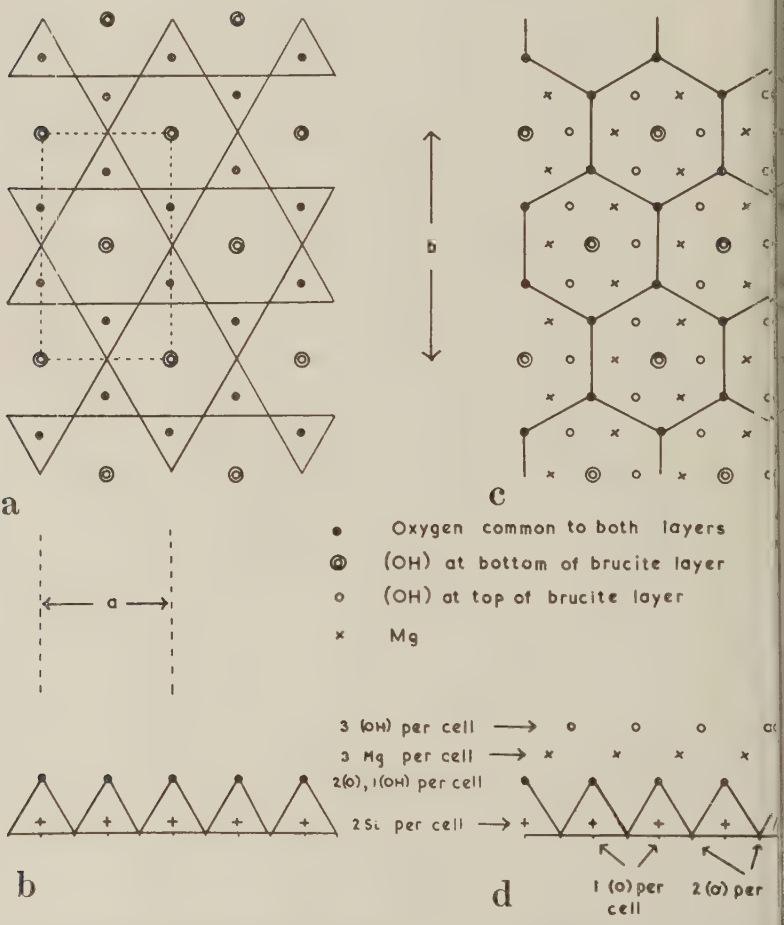

FIG. 1. (*a*) Tetrahedral Si_2O_5 network in plan. (*b*) Tetrahedral network as viewe along '*b*'-axis. (*c*) Tri-octahedral layer. (*d*) Chrysotile layer.

CURVED SHEETS.

It has been shown conclusively (Aruja 1943, Whittaker 1953) tha the structure of chrysotile asbestos is essentially of the layered typ illustrated in fig. 1. As with kaolinite, each layer consists of a tetra hedral Si_2O_5 network (shown *a* in plan, and *b*, as viewed along th '*b*'-axis), above which lies *c*, an octahedral layer, the two parts sharin

plane of O and (OH) ions. The '*b*'-axis projection of the composite layer is shown in fig. 1*d*.

Pauling (1930) predicted that such a composite sheet could exist only if curved, since the natural repeat distance in the brucite layer (5·4 Å.) is greater than that in the tetrahedral layer below it. The X-ray work of Aruja and of Whittaker, and electron micrographs by Bates, Sand, and Mink (1950), and by Noll and Kircher (1951), have shown that this curving does in fact occur in chrysotile asbestos, forming cylindrical tubes by bending of the sheet about the '*a*'-axis. But there appears to be no convincing reason why bending about some other crystallographic direction should not occur. If about the 9·2 Å. axis the effect would be to make this the fibre axis repeat distance instead of 5·3 Å.

An X-ray examination of several varieties of coarsely fibrous serpentine minerals showed that this fibre axis does frequently occur (Zussman, 1953). Fibre photographs have been taken of specimens belonging to either of the two Selfridge groups. Those classified as 'serpentine' were found to have a fibre axis repeat distance of approximately 5·3 Å., while the antigorites have 9·2 Å. The specimens exhibit differences of colour and/or texture and are listed in table II, using the names by which they were described in the museum collections from which they were obtained.

TABLE II. Fibre axis repeats in serpentine specimens.

Reference no.*	Specimen.	Repeat distance along fibre axis (in Å.).
O. 19376	Serpentine asbestos (Shabani mine, Southern Rhodesia)	5·3
O. 16328	Serpentine (New York)	5·4
O. 1899	Serpentine (Montville, N.J.)	5·3
O. 9652	Schweizerite (Zermatt)	5·3
O. 3930	Schweizerite (Zermatt)	5·3
B.M. 47963	Marmolite (Hoboken, N.J.)	5·3
B.M. 1908.97	Metaxite (Saxony)	5·3
M. N.2522	Serpentine (Montville, N.J.)	5·3
O. 16336	Picrosmine (Tyrol)	9·2
C. T.W.2915	Picrolite (Taberg, Sweden)	9·3
C. T.W.2914	Antigorite (Shipham Range ?)	9·2
C. 19343	Antigorite (Hokitika, N.Z.)	9·2
C. 19544	Picrolite (locality ?)	9·2

* The prefixed letters O, B.M., C, and M indicate that the samples were obtained from mineral collections of the Oxford University Museum, the British Museum, the Cambridge University Department of Mineralogy and Petrology, and the Manchester Museum, respectively.

The work of Hess, Smith, and Dengo (1952), Nagy (1953), Roy a
Roy (1953), and others, has suggested, and in some cases demonstrat
that the occurrence of a platy rather than a fibrous habit in a serpen
mineral is associated with certain features of its chemical composit
e.g. replacement of Mg or Si by Al, or a high (Si,Al):(Mg,Al) ra
Either of these would serve to produce a better fit between compone
of a layer and hence reduce its tendency to curve. It would seem r
that two minerals with identical composition involving a certain deg
of curvature may yet appear dissimilar through having a different a
of curving (fibre axis). The occurrence of one fibre axis rather than
other in such a case may be a consequence of physical conditions at
time of crystal growth.

Plausible structures.

The possibility of curvature about the '*b*'-axis suggests an explan
tion of the large '*a*'-axis of antigorite (Mikonui) in terms of a corruga
sheet. A model of this sort was described by L. Onsager.[1] It has a
alternating wave nature of periodicity 43·5 Å., the polar sheet inverti
at each line of inflexion. Both this and another similar model, to
described later, would be consistent with other observed features suc
as:

1. Some similarity between the structures of antigorite and chrysotil
   particularly in the '*c*'-direction.
2. The (100) cleavage noted in the single crystal. (Lines of inflexio
   will probably involve some discontinuity and therefore weakness
3. Streaky diffraction spots when $k \neq 3n$, where n is an intege
   (Randomness of stacking can easily occur by displacements
   layers in the '*b*'-axis direction.)

But it is clearly desirable that more direct evidence be obtaine
ideally the complete matching of the diffraction intensities with tho
derived from a trial structure. The remainder of this paper is concern
with an attempt to approach this goal.

The X-ray data.

One prerequisite for a more complete analysis was the production
clearer X-ray photographs. Complicating features of those obtained b
Aruja are the extra spots given by misoriented fragments, and t

[1] Reported in summarized proceedings of a conference on the structures of silica
minerals (Robinson and Shaw (1952)), and described by Prof. Onsager in priva
communication.

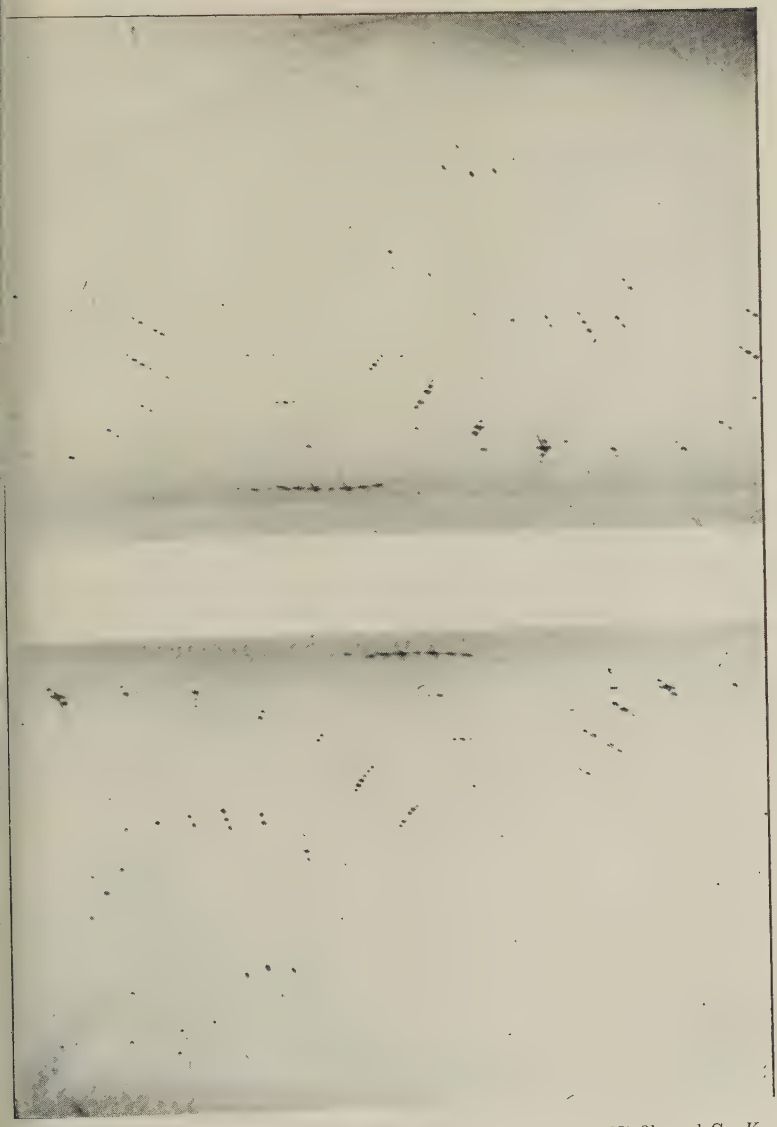

FIG. 2. Antigorite (Mikonui). Weissenberg ($h0l$) photograph. Ni filtered Cu-$K\alpha$ radiation.

fuzziness of Weissenberg photograph reflections tending to merge ther where they are closely spaced. A small crystal ($0{\cdot}25 \times 0{\cdot}1 \times 0{\cdot}07$ mm has been found which gives photographs almost free from these defec- *h0l* reflections only were recorded with a Weissenberg camera using N filtered Cu-$K\alpha$ radiation, exposure times varying from 10 minutes t 24 hours (fig. 2). Intensities were measured visually and correctio applied for Lorentz and polarization factors but none for absorpti effects.

From fig. 2 it can be seen that all reflections with the exception o some at high angle are clearly resolved and sharp. The reflections fr a small misoriented fragment do not interfere with the main arra Low-angle reflections, not shown here, were recorded on other pho graphs taken with the beam-trap off-set.

The nature of this diffraction pattern can be better evaluated b reference to fig. 6, which contains a diagrammatic representation of th weighted reciprocal lattice. In this diagram vertical black strokes ar drawn at points of the reciprocal lattice, the length of a stroke bein made roughly proportional to the observed intensity of the correspond ing X-ray reflection.

Clusters of reflections tend to occur around points with $h = 16n$ o $17n$ (n = integer), i.e. on the sub-cell reciprocal lattice, but, as Aruj pointed out, maxima do not always occur at the centre of a group, an neither maxima nor geometrical centres of groups occur at strictly con stant h values. The number of reflections in a group varies in an appa rently irregular manner.

Trial structures.

A type of corrugated sheet which departs as little as possible fron planarity is that illustrated in fig. 3*a* (compare fig. 1*d*) and is referre to henceforth as the 'rectified wave' model. This shows one cell of th proposed structure as viewed along the '*b*'-axis. In order that the ce shall have $a = 43{\cdot}5$ Å. it must contain $8\frac{1}{2}$ repeats of the sub-cel (5·3 Å.) along the curve (9 repeats would require an unduly small radiu of curvature). A way in which this might reasonably occur was sug gested by Onsager for his 'alternating wave' model in which, at a inversion, a system of 8- and 4-membered rings occurs instead of th usual hexagonal network of the tetrahedral layer (fig. 4). This introduce an additional 5·3/2. On building a 'ball and spoke' model it was see that this 8:4 ring system is possible even where no inversion of the layer occurs, provided that small departures from normal bond angle

are allowed. If such a mechanism is employed at each discontinuity of the rectified wave, a model consistent with the cell dimensions results. In the 'alternating wave' model the 8:4 ring system can be assumed only at every other inversion if an $8\frac{1}{2}$-fold axis is to be explained.

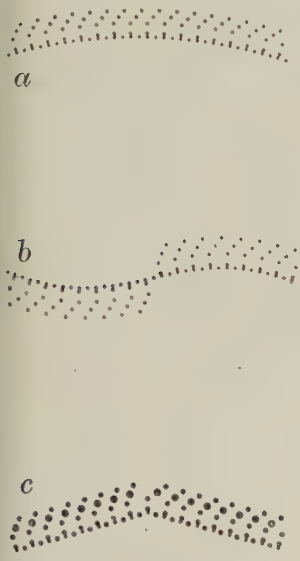

Fig. 3.

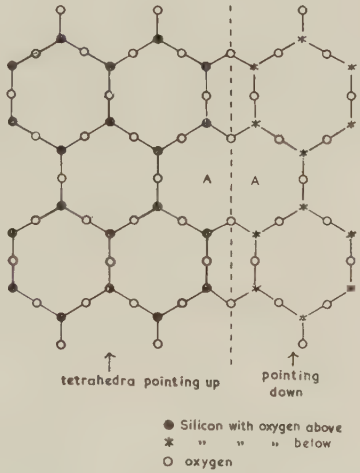

Fig. 4.

Fig. 3. (*a*) One cell content of 'rectified wave' structure.
(*b*) „ „ „ „ 'alternating wave' structure.
(*c*) „ „ „ „ 'zig-zag' structure.

Fig. 4. System of 8- and 4-membered rings in tetrahedral silicate layer.

The diffraction spectroscope.

A method for rapidly testing trial structures has been developed at the Physics Department of the Manchester College of Technology. A full description is given in various papers, Hughes and Taylor (1952), Hanson, Lipson, and Taylor (1953), Hanson (1953), and an abstracted version is presented in the following paragraphs.

Use is made of the similarity between two phenomena: the diffraction of light by a set of holes, and the diffraction of X-rays by a set of atoms. The optical apparatus is illustrated in fig. 5. Monochromatic light from a source *A* is focused at a pinhole *B*. The divergent beam is rendered parallel by lens *C* and brought to focus by *D* in the plane *F* after reflection at mirror *E*. If a card containing a set of holes is placed at *O* the

diffraction pattern produced is focused in the plane F, where it may be viewed through a microscope or photographed.

The X-ray diffraction pattern is a 3-dimensional one, but that part of it in the equatorial plane (the $h0l$ reflections in the present case) depends only upon the x and z atomic co-ordinates, i.e. upon a projection of the atomic positions on to the xz plane.

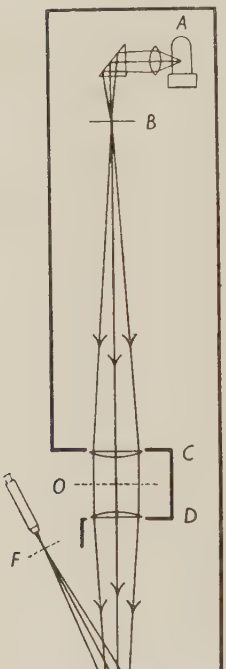

FIG. 5. Schematic representation of diffraction spectroscope. (Taylor, Hinde, and Lipson, 1951.)

The projection is drawn on a large scale and rapidly transformed into a punched mask by means of a specially constructed reducing pantograph. The optical diffraction pattern produced, called the 'optical transform', is photographed and can then be compared with the X-ray data of the weighted reciprocal lattice drawn to the correct scale and superimposed.

The first model tested by this method was one of a single cell of the rectified wave type, using a radius of curvature of approximately 60 Å. and the z co-ordinates given by Aruja (1943) for chrysotile. The centres of different scattering power corresponding to single, double, and triple oxygen, double silicon, and triple magnesium ions were simulated by holes made with punches of different sizes. Fig. 6 shows the optical transform of this model with weighted reciprocal lattice superimposed. The two patterns should be compared at reciprocal lattice points, since it is only there that X-ray intensities are observed. (Adding a large number of cells to the model would not affect the relative intensities at lattice points, but would give an optical transform with lower intensity between them.)

A qualitative similarity between the two transforms can at once be recognized, but they differ in two important respects. The fan-shaped regions of high intensity in the optical transform have a wider angular spread than those of the X-ray pattern, and the maxima of the former are more closely spaced along the a^*-axis. Both of these features were taken to indicate that a larger radius of curvature was required, and the effect of making this change to $R = 100$ Å. is shown in fig. 6*b*. The value of R, which was judged to give the best correspondence, was 85 ± 5 Å.

An attempt was next made to discover how successive sheets of the structure are stacked, since there are two ways in which the β angle can be produced. Masks were punched containing 5 unit cells in the 'c'-axis

Fig. 6*a*. Optical transform of single cell of 'rectified wave' structure with radius of curvature $R = 65$ Å. Superimposed is a weighted reciprocal lattice corresponding to the X-ray data.

Fig. 6*b*. The same, with $R = 100$ Å.

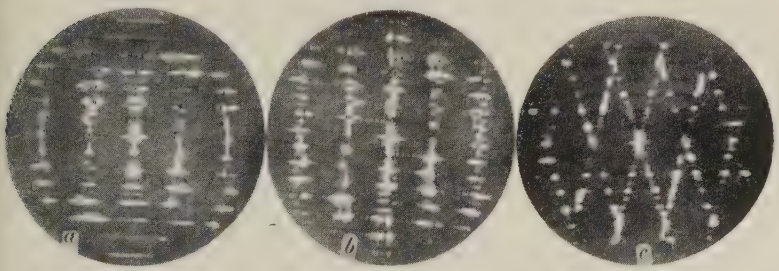

Fig. 7*a*. Optical transform of 5 cells of 'rectified' structure.
Fig. 7*b*. „ „ „ „ „ 'alternating' structure.
Fig. 7*c*. „ „ „ „ „ 'zig-zag' structure.
Each has the weighted reciprocal lattice superimposed.

direction, arranged to represent the two possibilities and at the same time enabling a more accurate representation of the scattering powers of the different ions (see Hanson 1953).

The 'optical transform' (fig. 7*a*) which fitted the X-ray data was that from the structure with β angle as illustrated in fig. 8 (similar to that of clino-chrysotile, Whittaker 1953).

Trial was then made of the 'alternating wave' structure (fig. 3*b*) using a radius of curvature of 40 Å. so that the 'peak-to-valley' distance was approximately 3·5 Å. Its optical transform did not appear to fit the X-ray data at all closely, but considerable improvement was obtained by using instead a radius of 65 Å. The transform obtained using this value is shown in fig. 7*b*.

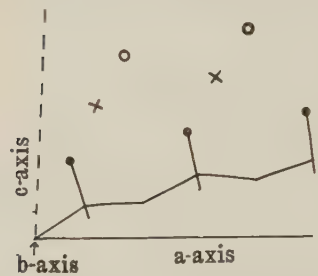

FIG. 8. Mode of stacking of successive layers. Symbols as in fig. 1 (p. 500).

A further possible though unlikely corrugated structure which does not involve curving of the sheets is the zig-zag arrangement of fig. 3*c*, and its optical transform is shown in fig. 7*c*.

It should be noted that the large cell-size of antigorite imposes a severe test on the optical system of the instrument, whose imperfections are shown by the extent to which the transforms lack centro-symmetry.

POWDER PHOTOGRAPH AND CHEMICAL ANALYSIS.

Powder photographs were taken using a 9-cm. camera and Ni filtered Cu-$K\alpha$ radiation. The derived interplanar spacings and visually estimated intensities are compared in table III with data given by Hess, Smith, and Dengo (1952), for antigorite from Caracas, Venezuela. The similarity of the two sets shows that the varieties have similar crystal structures, and the presence of the large cell in the Caracas variety is additionally indicated by the low-angle lines of spacing 5·78 to 6·95 Å. which were observed using a counter spectrometer.

Dr. R. A. Howie was able to separate a small amount of pure antigorite from the rock, and carried out a chemical analysis in this department the results of which are compared in table IV with that published by Hess, Smith, and Dengo for antigorite from Caracas, Venezuela. The latter workers first derived the formula $(Si,Al)_{4\cdot16}(Mg, \&c.)_{5\cdot88}O_{10\cdot43}(OH)_{7\cdot57}$ which was based upon 18(O,OH) ions. Observing that this departed considerably from the ideal serpentine formula $Si_4Mg_6O_{10}(OH)_8$, and that Mg:Si ratio was close to 7:5, they recalculated assuming this ratio, and derived the formula $(Si,Al)_{4\cdot97}(Mg, \&c.)_{7\cdot03}O_{12\cdot95}(OH)_{8\cdot05}\cdot 1{\cdot}4H_2O$, which approximated to the general formula $Si_5Mg_7O_{13}(OH)_8\cdot nH_2O$.

Brindley (1954) has criticized this procedure, pointing out that the analysis may be recalculated on the basis of 2Si ions, resulting in the formula $Si_2(Mg, \&c.)_{2\cdot927}O_{5\cdot105}(OH)_{3\cdot720}$ which departs little from the

ideal for serpentines by having small deficiencies in Mg and (OH) ions. It was suggested also that the excess of O above 5 may be due to a process of dehydration.

TABLE III. X-ray powder patterns of antigorite.
1, Caracas, Venezuela (Hess, Smith, and Dengo). 2, Mikonui, New Zealand.

1.		2.		1.		2.	
d(Å.).	Int.	*d*(Å.).	Int.	*d*(Å.).	Int.	*d*(A.).	Int.
8·05	10	—	—	1·781	14	1·780	—
7·30	400	7·28	9	1·755	4	—	3
6·95	24	—	—	1·736	10	1·740	1
6·51	16	6·46	½	1·688	2	—	—
6·10	6	—	—	1·640	2	—	—
5·78	8	5·82	½	1·584	3	—	—
4·67	6	4·64	3	1·560	12	1·554	5
4·62	7			1·540	9	—	—
4·27	4	4·26	2	1·535	9	1·533	4
4·01	6	3·91	1	1·524	13	1·517	2
3·63	300	3·60	8	1·509	8	1·500	2
3·51	24	—	—	1·497	10	1·492	1
2·88	2	—	—	1·479	7	1·477	1
2·59	4	2·58	2	1·466	6	1·461	1
2·57	8			1·462	6	—	—
2·52	70	2·51	10	1·451	10	1·447	1
2·46	9	2·45	3	1·448	9	—	—
2·42	38			1·443	5	—	—
2·39	9	2·39	2	1·438	3	—	—
2·35	5	2·31	½	—	—	1·415	½
2·237	6	2·24	½	1·339*p*	—	1·339	½
2·208	7	2·209	1	1·328	—	—	—
2·167	22	2·169	5	1·314*p*	—	1·315	4
2·150	20	2·153	3	—	—	1·300	1
2·126	4	2·121	¼	—	—	1·289	½
2·035	4	—	—	1·279*p*	—	1·280	1
1·886	3	—	—	1·261*p*	—	1·264	1
1·830	12	1·831	2	1·209*p*	—	—	—
1·815	23	1·811	1				

All lines in column 1 except those marked *p* were recorded by Geiger counter spectrometer. Intensity estimates are on different arbitrary scales.

TABLE IV. Chemical analyses of antigorite.
1, Caracas, Venezuela (Analyst, L. C. Peck in Hess, Smith, and Dengo, 1952).
2, Mikonui, New Zealand (Analyst, R. A. Howie).

	1.	2.		1.	2.
SiO_2 ...	43·60	43·45	MgO ...	41·00	41·90
TiO_2 ...	0·01	0·02	CaO ...	0·05	0·04
Al_2O_3 ...	1·03	0·81	Na_2O ...	0·01	0·05
Cr_2O_3 ...	0·02	n.d.	K_2O ...	0·03	0·02
Fe_2O_3 ...	0·90	0·88	H_2O+	12·18	12·29
FeO ...	0·81	0·69	H_2O-	0·08	0·04
NiO ...	0·16	n.d.		99·92	100·19
MnO ...	0·04	nil	Sp. gr....	2·607	2·60 (Aruja, 1944)

In the present investigation, knowledge of the cell dimensions and density of the crystalline material allows the derivation from the analysis of absolute values for the atomic proportions, which are independent of structural assumptions. The cell content is seen to be:

$$\underbrace{(Si_{33\cdot2},Al_{0\cdot7})}_{33\cdot9}\underbrace{(Fe'''_{0\cdot5},Fe''_{0\cdot4},Mg_{47\cdot7},Ca_{0\cdot3})}_{48\cdot9}H_{62\cdot6}O_{148},$$

which is consistent with the following sequence of atoms in successive curved planes: 51(O), 33·9(Si,Al), 34·4(O) and 15(OH), 48·9(Mg, &c.), 47·6(OH).

The crystal structure proposed involves $8\frac{1}{2}$ repeats of the sub-cell in the tetrahedral layer, i.e. 34 Si atoms per cell. It may also be noted that the 'rectified wave' model clearly implies a deficiency of Mg and (OH) ions, since at the junction of neighbouring 'arches' there is insufficient room for an extra half sub-cell in the octahedral layer. Moreover, the two (OH) ions at the top of the tetrahedral layer in positions marked A (fig. 4) would be unduly close to one another and would probably also be omitted. Allowing for these deficiences, the numbers of atoms in successive planes would be as follows: 51(O), 34Si, 34(O) and 15(OH), 48Mg, 48(OH). The structural model is thus in accord with the chemical data and with the observed density, within the limits of experimental error.

Assuming that the Caracas variety has cell dimensions very close to those of the Mikonui antigorite, and using the observed density value 2·607, its cell content may be derived from the analysis as:

$$\underbrace{(Si_{33\cdot1},Al_{1\cdot0})}_{34\cdot1}\underbrace{(Fe''_{0\cdot6},Fe'''_{0\cdot5},Mg_{46\cdot9},Ni_{0\cdot1})}_{48\cdot1}H_{62\cdot4}O_{147\cdot3},$$

corresponding to the sequence 51(O), 34(Si,Al), 33·9(O) and 15(OH), 48·2Mg, &c., 47·4(OH), which compares favourably with that calculated from the Mikonui analysis, and with that of the structural model.

It would seem that the correct way to treat the Caracas data would be by an extension of Brindley's method, whereby some of the Al is grouped together with Si, and then the formula calculated to make (Si+Al) equal 2. This could perhaps not have been justified in the absence of other data, but it is interesting to note that this allocation shares the trivalent ions equally among 'octahedral' and 'tetrahedral' sites.

Summary and conclusions.

The 'optical transform' method has been used to support the theory that a curved and corrugated-sheet structure exists in the crystals of antigorite studied. It is not possible to decide at present which of two types of corrugation is correct, an 'alternating wave' with radius approximately 65 Å. or a 'rectified wave' with $R \sim 85$ Å., although the latter seems to be structurally more plausible. The manner in which successive layers are stacked has been determined.

The present investigation indicates only the broad lines on which the structure is based and little can yet be said about the detail of structure at the junction of neighbouring 'arches', particularly with regard to the octahedral layer. Using one of the proposed structures, however, it may be possible to initiate, in the case of the correct one, a series of 'Fourier refinements' leading to an electron density map.

Chemical formula, and the measured density, are consistent with the proposed structure: furthermore, analysis, density, optics, and powder photograph indicate that the antigorite from Caracas studied by Hess, Smith, and Dengo is essentially the same as that from Mikonui, possessing the large cell and, it is here suggested, the corrugated-sheet structure. It would appear, then, that small deficiencies in Mg (as compared with the ideal serpentine), and small replacements by Al, may result in a tabular rather than fibrous morphology by means of the super-cell described, and not necessarily through reducing the sheet curvature.

Brindley (private communication, Nov. 1953) has described another variety of antigorite from Unst, Shetlands, which has a 43·8, b 9·22, c 14·53 Å. and is orthorhombic. Thus the 'large cell' variety, which has hitherto been regarded as anomalous and non-representative of the antigorite group, may in fact be typical. The evidence for the existence of curved sheets in the platy crystals makes it seem most likely that the coarsely fibrous varieties of antigorite also have the sheet structure, curved about the 9·2 Å. axis. These and other varieties, including that from the type locality Val Antigorio, Piedmont, may all embody the Mikonui structure but with varying degrees of perfection.

Finally, it is hoped that this investigation has demonstrated the usefulness of the diffraction spectroscope for rapidly testing complex variants of a basic structure in an attempt to explain unusual diffraction effects.

Acknowledgements.—The author wishes to record his thanks to Professor C. E. Tilley, Professor L. R. Wager, Dr. R. M. C. Eagar, and the

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An accessory to the polarizing microscope for the optical examination of crystals.

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QUALITATIVE studies of the optical properties of crystals under the polarizing microscope and refractive index measurements by immersion methods are made on slides placed upon the microscope stage. These procedures have the disadvantage that the crystals have a fixed orientation. Quantitative properties, such as optic axial angles, are measured on an accessory to the microscope, such as the universal stage, which although allowing rotation of the crystal necessitates auxiliary stereographic projection and is often considered laborious in operation and is not widely employed.

The single instrument to be described overcomes some of these limitations, yet is simple in construction and easy to operate. In the study of individual crystal grains or small sections of aggregates in liquid or solid mounts it may be used for work covering qualitative observations and measurements of principal refractive indices, optic axial angles, orientation, and essential optical properties. Stereographic projection is avoided. The crystal rotates freely to give any desired orientation during observations.

The device is used in conjunction with a polarizing microscope and consists essentially of a glass sphere, base-plate, disk, and markers, as shown in the diagram (fig. 1).

The crystal grain under observation is mounted at the centre of the sphere, A, of about 2·5 cm. in diameter, formed of two segments of optical glass of a chosen refractive index, which are readily detached and reassembled. This feature is achieved by cementing a thin, flat metal ring to the plane surface of each segment, the ring of one segment being an accurate fit within that of the other. When the segments are placed together they form a true sphere and the outer metal ring constitutes part of the spherical surface. The plane surfaces of the two segments are separated by a space of about 0·5 mm. within which the crystal is mounted. The sphere rotates freely on a three-point support, of hardened, polished steel balls in a central opening, B, in the

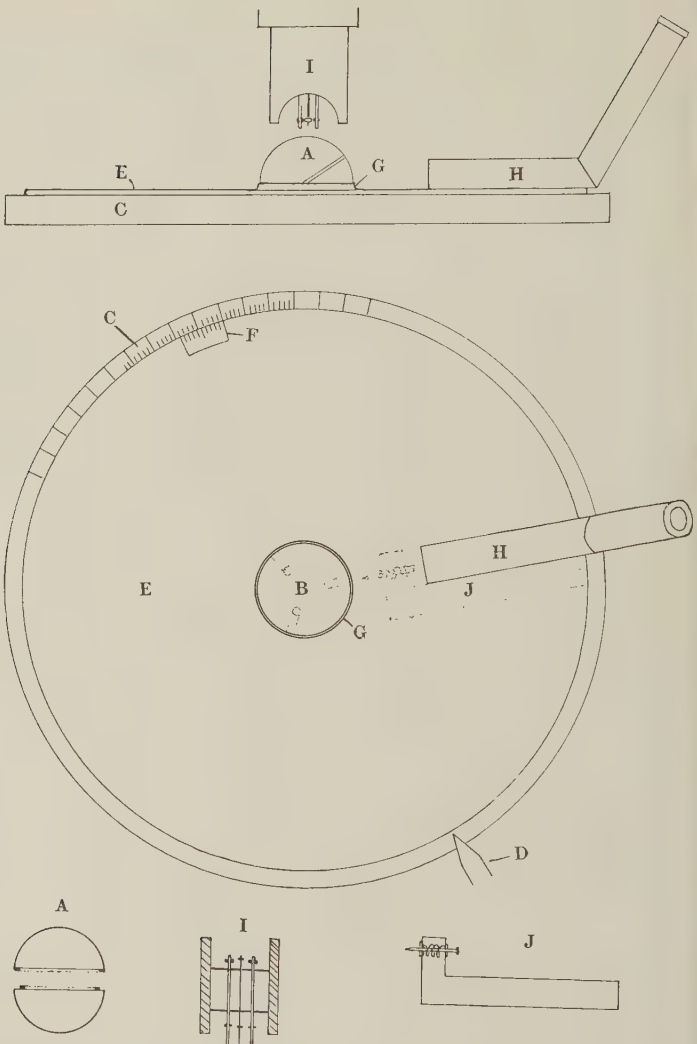

FIG. 1. Accessory to polarizing microscope.
A sphere, B central opening, C base-plate, D fixed reference pointer, E disk, F vernie
G collar, H reading microscope, I objective marker, J horizontal marker.

base-plate, C, the outer rim of which is marked with a scale of degrees ar
is fixed to and rotates with the microscope stage. Base-plate rotation
are read on the rim against a fixed reference pointer, D. The disk, I
is set into and revolves upon the base-plate and its angular movemen

are read by means of a vernier, F, against the scale of the base-plate. The disk has a circular central opening bordered by a collar, G, the rim of which defines the horizontal great circle or equator of the sphere. The pole of this great circle lies on the axis of the microscope and is coincident with the cross-hairs. The disk is fitted with a small horizontal reading microscope, H, provided with cross-hairs adjusted to the equator of the sphere.

The microscope stage itself may be used as the base-plate if suitably modified to take the disk and the sphere supports.

The objective marker, I, which, when in use, occupies the position of the microscope objective, operates on lowering the tube. Vertical needles, tipped with pigment, contact the sphere and rise in their guides. A mark of microscopic dimension is thus made on the sphere at its pole lying at the intersection of the cross hairs, between two dots, easily located by the naked eye, which serve to indicate by their alignment the vibration directions within the crystal.

The horizontal marker, J, moves on the disk, against a slide on the reading microscope. It carries a spring-loaded needle, which operates through a notch in the collar of the disk. It is used to plot points, coincident with the cross-hairs of the reading microscope, on the equator of the sphere, at known angular distances apart, corresponding with vernier readings.

The base-plate, once fixed and centred, need not be detached. For conventional slide studies, sphere and disk only need to be removed.

Crystal material for study as grains or aggregates is mounted in the sphere on or between cover-glasses, in liquid or solid media. When principal refractive indices and other optical properties are to be determined at one time, mobile immersion liquids are used. For this purpose scattered grains are caused to adhere lightly to a cover-glass by a thin film of adhesive. The cover-glass is then attached to the plane surface of one hemisphere by means of a viscous medium, sufficiently mobile to allow it to be moved laterally and thus permit a grain to be selected and centred for study. A cover-glass is attached to the opposite hemisphere, a minimum of chosen liquid is applied to the grains, and the segments are then assembled. The choice of media is of course influenced by solubility relationships, and the refractive index of all the materials comprising the mount must be taken into account if total reflection effects are to be avoided. The immersion medium is held by surface tension at the central area of the sphere, the construction of which allows the liquid to be changed without disturbing the selected grain.

Specimens for study must have clearance in the space provided between the cover-glasses.

A low-power condenser of appropriate focal length, adjustable in height below the stage, provides parallel or convergent light. The Bertrand lens, fitted with an iris diaphragm, should be capable of being focused in the tube. For conoscopic observation without the ocular a loosely-fitting cap, drilled with a central pin-hole, gives improved definition. Strong illumination is necessary, especially when working with small grains. The lamp should be fitted with an iris diaphragm so that the image of the source shows as a circular patch of illumination at the centre of the sphere, and may be adjusted in size by the diaphragm, and limited to the area of the centred crystal under observation.

For qualitative work the convergent phenomena and other optical characters of the crystal may be studied for any desired orientation by revolving the sphere in its seating and by rotating the base-plate, or by a combination of both. For quantitative observations, points of emergence of optical directions in the interference figure, such as the optic axes, are adjusted to the cross-hairs of the microscope and the objective marker is brought into operation to plot the corresponding points on the sphere, which, with its inscribed angular relationships and other data, and the crystal at its centre, represents a model of the indicatrix of the crystal.

In measurements carried out on the sphere, only simple great circle and polar relationships are involved. Thus, when the sphere is manipulated to bring the optic axial plane, indicated by the two plotted optic axial points, to the equator (defined by the collar of the disk) an axis of the indicatrix emerges at the pole of the sphere, coinciding with the cross-hairs of the microscope and this may be plotted on the sphere.

In order to measure the angle between two plotted points the sphere is adjusted to bring them on to the equator. The angular separation of the points is given by the difference in vernier readings when the cross-hairs of the reading microscope are moved from one point to the other. A reference line on the collar may be used instead of the reading microscope when approximate measurements are needed.

Points may be plotted and angles set off upon the sphere along its equator using the horizontal marker. In addition, small angles on great circles between points on the sphere may be measured utilizing a micrometer ocular, the divisions of which are calibrated in terms of degrees on the sphere. These angles may be set off and plotted by the

objective marker. Refractive index corrections necessitated by refraction effects of the glass may therefore be carried out on the sphere itself without recourse to stereographic projection. Points of emergence of optical directions, such as optic axes and indicatrix axes, once plotted, are available to indicate positions for refractive index observations by the immersion technique.

The mobility of the sphere is an advantage in the total-reflection method for the estimation of the refractive indices of liquids and platy crystals mounted in the sphere. The illumination boundary, corresponding to the vibration direction concerned, is adjusted to the cross-hairs of the microscope, and the critical angle plotted on the sphere and measured along the equator.

For demonstration, and as an aid in locating optical directions, the interference figure may be seen by normal vision when projected on to a ground glass screen held at the position of sharpest definition. By rotation of the sphere the phenomena may be located and brought into any desired position.

The sphere may be reversed to obtain the mean of two sets of readings, to improve accuracy in quantitative work.

The significance of tridymite in igneous and metamorphic petrogenesis.

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1. Introduction.

PHYSICO-CHEMICAL data clearly show that the presence of tridymite in a rock indicates the prevalence not only of high temperatures, but also of relatively low pressures during the formation of that rock. Whereas many authors (e.g. Shand, 1927; Larsen, 1936) have used tridymite as an indicator of temperature, the importance of tridymite as an indicator of pressure has been largely overlooked.

Although the presence of tridymite is by itself sufficient to enable the pressure, and hence the depth, at which a rock formed to be estimated within certain limits, the presence of tridymite in association with some other pressure- or temperature-indicating mineral allows much closer limits to be set.

2. The physico-chemical data.

a. The stability field of tridymite.

Recent and accurate work by Mosesman and Pitzer (1941) permits the calculation, within definite limits of error, of the rates of variation of the inversion temperatures with pressure for the various forms of silica. This calculation is based on the Clausius equation

$$dT/dP = T(\Delta V)/q,$$

where dT/dP is the rate of change of the inversion temperature with pressure: T is the transition temperature on the absolute scale (°K.) ΔV is the change in volume during the transition: and q is the heat change involved in the inversion. For the inversion of 1 mole of silica from quartz to tridymite Mosesman and Pitzer found the following values: T = 867° C. = 1140° K.; V = 3·75 c.c. and $q = 120 \pm 5$ calories; corresponding to which dT/dP lies between the limits 1·476° C. and 0·608° C. per atmosphere increase in pressure, the most probable value being 0·861° C. per atmosphere.

Mosesman and Pitzer's values relating to the transition of tridymite to cristobalite are: T = 1470° C. = 1743° K.; V = ∼−0·1 c.c.; and

$V = 50 \pm 50$ calories. For this inversion dT/dP lies between the limits $-\infty$ ° C. and $-0{\cdot}0421$° C. per atmosphere increase in pressure, the most probable value being $-0{\cdot}0842$° C. per atmosphere: Mosesman and Pitzer state that dT/dP is definitely negative.

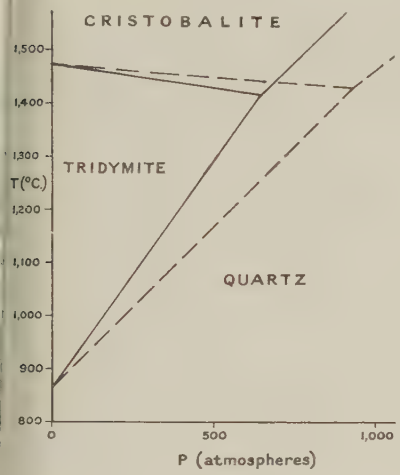

Fig. 1.

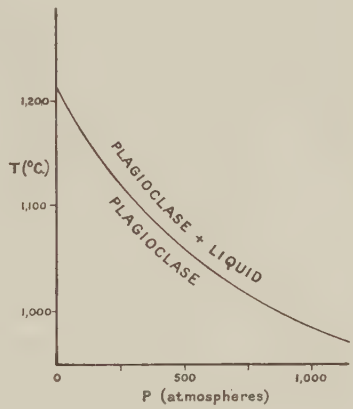

Fig. 2.

Fig. 1. The stability field of tridymite. The phase boundaries shown in unbroken lines are those derived from the most probable values of dT/dP; those shown in broken lines have been derived from values of dT/dP selected so that the tridymite field reaches its greatest possible extent.

Fig. 2. Curve showing the probable variation in the temperature of incipient fusion of An_{35} with pressure.

Bridgeman's researches (1949) have shown that the values for dT/dP do not vary significantly with considerable increase of pressure: the above data are therefore sufficient to determine the stability field of tridymite. If the most probable values of dT/dP are selected, the quartz-tridymite boundary is the straight line $0{\cdot}861P - T = -867$ and the tridymite-cristobalite boundary is the straight line

$$0{\cdot}0842P + T = 1470$$

where P is the pressure and T the temperature.[1] The triple point quartz-tridymite-cristobalite lies at the intersection of these two lines; its co-ordinates are therefore 640 atmospheres and 1415° C. (fig. 1). Below

[1] These equations relate pressure in atmospheres with temperature in degrees Centigrade.

this pressure tridymite can form quartz, above it quartz inverts directly to cristobalite.

If values for dT/dP are selected from the limits given above so that the stability field of tridymite reaches its greatest possible extent, the quartz-tridymite and tridymite-cristobalite boundaries are the lines $0{\cdot}608P - T = -867$ and $0{\cdot}0421P + T = 1470$ respectively: the triple point now occurs at 930 atmospheres and 1430° C. A pressure of 930 atmospheres is consequently the greatest possible pressure at which tridymite can form.

b. The variation in the fusion-point of plagioclase in the presence of water vapour with pressure.

The fusion point of albite decreases markedly with increasing pressure in the presence of water vapour (Goranson, 1938). The fusion point curve, at least for pressures greater than 500 atmospheres, has affinities with the curve of the adiabatic expansion of a perfect gas, $PV^{\gamma} = k$, where P is the pressure, V the volume, γ is the ratio of the two specific heats of the gas, and k is a constant. For pressures less than 500 atmospheres, however, the curve approximates closely to a straight line, $0{\cdot}310P + T = 1115$.

It is reasonable to assume that the temperature at which the sodic plagioclases commence to fuse in the presence of water vapour will also decrease with increasing pressure. A measure of this decrease can be obtained by comparison of the fusion temperature of albite with the temperature of incipient fusion of the plagioclase, both at a pressure of one atmosphere. For example, at this pressure, plagioclase of composition An_{35} begins to fuse at 1210° C. (Bowen, 1913), that is, 95° C. above the fusion point of albite. It is probable that the curve of the variation of the temperature of incipient fusion of An_{35} with pressure would, at least for relatively low pressures, parallel the fusion-point curve of albite but would, at any particular pressure, be at a temperature approximately 95 °C. higher. The curve of the incipient fusion of An_{35}, for pressures less than 500 atmospheres, would therefore be expected to approximate to the straight line $0{\cdot}310P + T = 1210$ (fig. 2). This curve intersects the quartz-tridymite phase boundary at a pressure which cannot exceed 375 atmospheres and is probably not more than 295 atmospheres (fig. 3).

3. Geological application of the data.

The greatest pressure under which tridymite can possibly form from quartz is less than 930 atmospheres and is probably not more than 640

atmospheres. These pressures would be reached under covers of 3850 and 2650 metres, respectively, of rock of specific gravity 2·5.

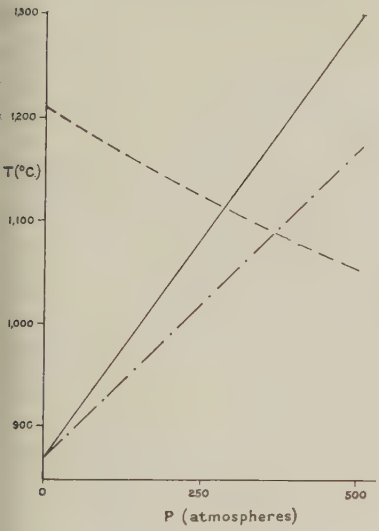

Fig. 3.

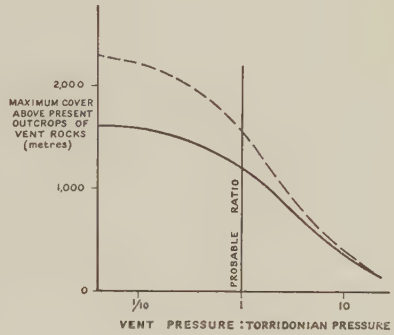

Fig. 4.

Fig. 3. Diagram showing the application of figs. 1 and 2 to the determination of the depth of formation of the present outcrops of the Tertiary vent in eastern Rhum. The solid line represents the most probable quartz-tridymite phase boundary and the dotted and dashed line the limiting position of this boundary (fig. 1). The dashed line is the variation of the incipient fusion point of An_{35} with pressure (fig. 2). If the pressure in the vent equalled that in the surrounding rocks, as appears probable, the pressure-temperature conditions in the vent and its neighbourhood must have fallen within the tridymite field (i.e. to the left of the quartz-tridymite phase boundary) very slightly above the incipient fusion curve of An_{35}. In consequence the maximum pressure cannot have exceeded 385 atmospheres and was probably less than 305 atmospheres, pressures which would be reached under covers of 1600 and 1250 metres of rock of specific gravity 2·5.

Fig. 4. Relation of maximum cover above present outcrops of the vent rocks and the ratio of vent pressure to Torridonian pressure. The solid line has been derived from the most probable tridymite field and the broken line from the greatest possible tridymite field.

Several occurrences of tridymite have been reported from the Tertiary complexes of Scotland. Harker (1950) has described tridymite-bearing hornfelsed sandstones from the aureole of the Rhum complex; Wager (1953*b*) has reported the existence of a tridymite-bearing granophyre in

the Skye complex; and Wells (1951) has described hypersthene-gabbro containing tridymite-bearing xenoliths from part of the Ardnamurchan complex. The tridymite now exposed in these rock masses must have crystallized at depths which certainly did not exceed 3850 metres and which were probably less than 2650 metres below the then existing surface.

The present author (Black, 1953) has described the occurrence in the east of Rhum of a small area of 'hybrid rocks', resembling marscoite between Tertiary gabbro and Torridonian sandstone. The Torridonian adjoining the 'hybrid rocks' has been intensely metamorphosed, with the production of abundant tridymite, while the 'hybrid rocks' themselves, interpreted by the author as the metasomatized infilling of a small vent, contain crystals of plagioclase (An_{35}) which have been very slightly fused; from petrological evidence the partial fusion appears to have occurred in the presence of water vapour. The outcrops of rock bearing partly fused plagioclase occur some 10 yards from the nearest outcrops of tridymite-bearing sandstone. The plagioclase crystals could not have been partly fused at a higher level in the vent and then introduced into their present position as this would imply that the vent temperature decreased rapidly with depth; on the other hand, if the fusion were effected at a lower level and the crystals then introduced from below, the estimates of the maximum depth at which the present outcrops of the 'hybrid rocks' formed would have to be correspondingly reduced.

The temperature and pressure in the vent and the adjoining rocks were such as to fall within the tridymite stability field very slightly above the curve of incipient fusion of An_{35}. If the pressures in the vent and in the surrounding Torridonian were equal, as appears to be probable, this curve lies within the tridymite field (fig. 3) only up to pressures which do not exceed 375 atmospheres and are probably no more than about 295 atmospheres — pressures which would be reached under covers of 1550 and 1200 metres, respectively, of rock of average specific gravity 2·5. If, however, the pressure in the vent differed from the pressure in the surrounding Torridonian these estimates of the maximum thickness of cover would have to be amended accordingly. The probable and possible maximum thicknesses of cover corresponding to a wide variation in the ratio of the vent pressure to the pressure in the Torridonian are shown graphically in fig. 4. The author considers it probable that the two pressures were approximately equal or that the vent pressure may have been slightly the higher.

The temperature in the vent was slightly greater than that required to produce incipient fusion in An_{35}, and, in consequence, the maximum possible pressure in the vent slightly exceeded the values quoted above, but, owing to the very small extent to which the plagioclase has been fused, the vent pressure, and hence the depth of formation of the now exposed vent rocks, could not have been significantly in excess of these values. The depth at which the presently exposed vent rocks were emplaced cannot therefore have exceeded 1600 metres and was probably less than 1250.

4. Conclusions.

Important integral members of the Tertiary complexes of Rhum, Skye, and Ardnamurchan were emplaced under covers whose tops were no more than 3850 metres and were probably less than 2650 metres above the present levels of erosion. A small Tertiary vent in the east of Rhum pierced a cover whose top was no more than 1600 metres and was probably less than 1250 metres above the vent rocks seen on the surface today.

The highest rocks preserved of the Rhum complex outcrop a short distance away from, and some 550 metres above, the tridymite-bearing Torridonian. These highest rocks and the gabbro responsible for the metamorphism of the Torridonian and the resultant tridymite form parts of the same rock mass and were presumably emplaced at the same time. The highest rocks now preserved on Rhum were therefore emplaced under a cover which cannot have exceeded 3300 metres and was probably less than 2100 metres. The vent exposures also lie 550 metres below the highest rocks now preserved on Rhum: the highest rocks were therefore not more than 1050 metres and probably less than 700 metres below the surface when the vent was active.

In a diagram accompanying a recent paper, Wager (1953*a*) shows the highest rocks at present preserved in the Rhum complex to have been at a depth of 8500 metres, this depth being necessitated by the hypothetical differentiation mechanism assumed to account for the rocks. The limiting thicknesses of cover consistent with the physico-chemical data are very much less than those envisaged by Wager.

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Rodingite from the Girvan-Ballantrae complex, Ayrshire.

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[Taken as read November 4, 1954.]

Occurrence and relationships. Altered and garnetized gabbros occur in association with serpentinite occupying the lower south-eastern slope of Byne Hill, one mile to the south of Girvan. The rocks crop out above Balaclava Wood near the footpath from Bynehill Bridge to Craiglea. Although the precise form of the altered gabbros is not very well revealed, they appear to be dikes intrusive into the surrounding serpentinized harzburgite. Contacts with the serpentinite are exposed in two places but are evidently lines of later movement. The relationships of these altered gabbros to the main gabbro mass of Byne Hill are obscure. They are, however, probably contemporaneous, since sporadic garnetization of the main gabbro occurs along its contact with serpentinite farther to the south-west.

Petrography. The rock is almost pure white and exceedingly tough, with a sharp flinty fracture. Dispersed aggregates of magnetite form the only conspicuous dark mineral. The high density (3·24) of the rock is a characteristic feature and distinguishes it from saussuritized gabbros.

Under the microscope the rock retains its original gabbroidal texture, but the plagioclase has been almost completely replaced by small colourless garnet with subordinate zoisite (fig. 1). The garnet averages 0·01 mm. in size and forms a dense matte rendering the plagioclase pseudomorphs isotropic. The altered plagioclase still preserves good crystal boundaries and is ophitically related to large plates of pyroxene almost completely altered to chlorite (pennine). Prehnite is generally present in the rock and parts of the dike may be almost wholly replaced by prehnite, together with pectolite and calcite.

Analyses. An analysis of a garnetized gabbro from Byne Hill is given in table I, A. This rock contained only minor amounts of prehnite. The most distinctive feature of the analysis is the low silica and high lime. The correspondence, both physically and chemically, with those garnetized gabbros known as 'rodingite' is evident (table I, B and C).

Nature of the garnet. Attempts to separate the garnet from the ro in quantities sufficient and pure enough for chemical analysis w unsuccessful due to the presence of zoisite which appeared to hav rather wide range of density. However, contamination with zoisite v

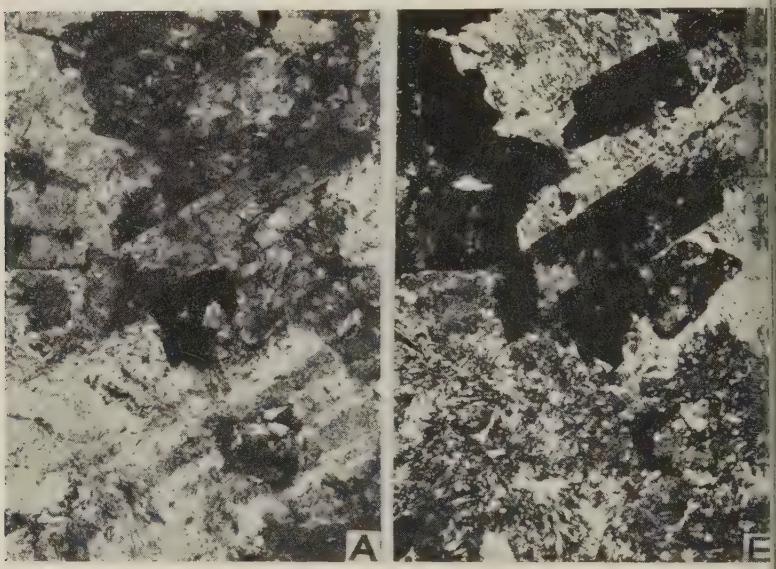

FIG. 1. Garnetized plagioclase and chloritized pyroxene. A large grain of magnetite at the centre. A, ordinary light; B, crossed nicols. ×15.

not serious enough to prevent the determination of the physical pr perties of the garnet which exhibited a range in density 3·49–3·3 (uncorrected values at room-temperature). Refractive index measur ments (Na-light) gave values of 1·742 with sp. gr. 3·49, and 1·718 wit sp. gr. 3·39. Garnet with the higher values of density and refracti index is grossular. That with the lower values may be a hydrogarn of the type described by Hutton (1943) from the New Zealand rodingite

Origin of the rodingites. The Byne Hill rodingite appears to be identic with those from New Zealand and Western Australia, all of which ar associated with ultrabasic rocks. Marshall (1911) regarded the rodin ites as primary products of crystallization, while Finlayson (190 considered that the basic magma had been enriched in lime by th digestion of limestone. Grange (1927) concluded that the rocks wer derived by the alteration and metasomatism of gabbros, the garn being secondary in origin. The source of the lime was ascribed to th

serpentinization of lime-bearing pyroxene in the adjacent ultrabasics (Grange, 1927; Miles, 1950; Watson, 1953).

TABLE I. Chemical analyses of rodingite.

	A.	B.	C.
SiO_2	38·04	33·95	40·98
TiO_2	0·82	0·42	1·01
Al_2O_3	15·07	19·91	12·77
Fe_2O_3	1·78	1·28	1·10
FeO	3·02	6·98	4·06
MnO	0·21	0·28	0·16
MgO	9·62	5·23	7·31
CaO	25·84	26·95	29·40
Na_2O	0·18	0·15	nil
K_2O	0·04		0·03
H_2O+ ...	4·19	4·85	2·68
H_2O- ...	1·15		0·31
CO_2	nil	nil	0·07
P_2O_5	0·24	—	0·08
	100·20	100·00	99·96
Sp. gr. ...	3·24	—	3·33

A. Rodingite, Byne Hill, Ayrshire, Anal. W. H. Herdsman.
B. „ Roding river, Dun Mtn., New Zealand. P. Marshall, 1911, p. 33.
C. „ Eulaminna, Western Australia. K. R. Miles, 1950, p. 125.

In addition to garnet, lime-bearing minerals (generally hydrous) include prehnite, pectolite, zoisite, epidote, and diopside (Watson, 1953), all of which are represented in other basic rocks marginal to serpentinite in the Girvan-Ballantrae district. The lime introduced into the Byne Hill rocks cannot have been derived from the serpentinization of the ultrabasics since the latter are dominantly harzburgites (olivine-bronzite). Some lime may have been available from the alteration of pyroxene and plagioclase in the gabbro itself, but would be quite subordinate in amount.

It is concluded that lime-rich hydrothermal solutions and CO_2, which immediately post-dated serpentinization, were responsible for the alteration of the gabbro and also produced local carbonatization ($CaCO_3$) of the serpentinite. Veins of diopside-zoisite traverse the serpentinite in some parts of the Girvan-Ballantrae district and are regarded as products of the same hydrothermal activity (Murgoci, 1900).

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A suggested igneous origin for the banded granular hornfelses within the hypersthene-gabbro of Ardnamurchan, Argyllshire.

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THE hypersthene-gabbro of Centre 2, Ardnamurchan, is intruded largely amongst sedimentary rocks. Despite this fact the majority of the inclusions are, as described by Richey and Thomas (1930), of granulitized basic and ultrabasic igneous rocks. Recently M. K. Wells (1951) studied this problem again, but was only able to find four occurrences in which the xenolith was undoubtedly of sedimentary origin. However, he considered in some detail a problematical group known as the banded granular hornfelses and concluded that, despite four possible modes of origin, the textural and compositional evidence favoured a development through the metasomatism of sediments.

The banded granular hornfelses are, according to Wells, generally characterized by a normal gabbroic suite of minerals, prominent concordant layering—often rhythmic and on a very fine scale, and a relative deficiency in clinopyroxene. These features typify rocks from certain horizons within layered basic intrusions, such as the rhythmically layered allivalites from the Isle of Rhum. Where these allivalites are caught up as inclusions within the later fine-grained gabbros, then the metamorphic sieve-texture of the olivines appears to replace the original poikilitic texture.

One diopside-bytownite-hornfels is described in detail (1951, pp. 731–732), Wells considering that the rock is of sedimentary origin because of its composition. An analysis is given, and though it is not compared directly with that of any other rock it is said to have features which the other hornfelses of this group lack—a composition closer, perhaps, to certain sediments of the marl or calcareous mudstone group than to any normal igneous rock.

A comparison of the chemical analyses of calcium-rich argillaceous sediments (e.g. Pettijohn, 1949) with that of the hornfels reveals certain major discrepancies. Most striking is the $K_2O:Na_2O$ ratio which is 2·5:1 in an average of 78 shales (Goldschmidt, 1954, p. 159) and, due

to its higher value in limestones (6·6:1), increases as the shale becomes more calcareous (e.g. the marl in table I). A further major difference lies in the proportion of Al_2O_3:SiO_2, which is abnormally high (0·52: in the hornfels. The average shale has an Al_2O_3:SiO_2 ratio of about 0·25:1, while that of the average limestone is 0·15:1 (Clarke, 1924, pp. 34, 564), the only argillaceous sediments with a much higher value being the residual bauxitic clays which are lime-free. Hence the simple metamorphism of any normal sediment could not produce the hornfels and Wells, drawing attention to the unusual K_2O:Na_2O ratios (1951, p. 733), suggests metasomatism as a means of explaining the difference in composition of sediment and hornfels.

In order to view the relationship between the composition of the hornfels and that of a normal igneous rock, similar analyses were examined amongst Washington's superior chemical analyses of fresh igneous rocks (1917). Though several similar analyses are to be found amongst the gabbros, an almost identical analysis (table I) is that of a Tertiary olivine-gabbro from the Cuillins, Isle of Skye. The chemical composition of the hornfels is closer to that of the Skye gabbro than to that of any normal sediment. Mineralogically the differences are not great, for the rock analysed by Pollard is better described as an olivine eucrite, low in olivine and having, in the CIPW norm, 79 % bytownite (An_{81}), 10 % diopsidic pyroxene, and 7 % olivine. The low silica content of the hornfels is, in view of the absence of olivine, probably due not only to the presence of 2·4 % normative ore but also to the epidotization which Wells comments upon.

Texturally the hornfels consists of layers of closely packed clino-pyroxene crystals separated by similar aggregates of bytownite crystals, the width of the layers varying from a millimetre to a centimetre. Such layering is a common feature of the ultrabasic rocks of Hallival and Askival, Isle of Rhum. There the layering, believed to be the product of a rhythmic deposition of crystals separating from a slowly-cooled basic magma, consists of a rapid alternation of crystals of bytownite, olivine, diopsidic pyroxene, and sometimes chrome-spinel. The formation of monomineralic layers is believed to be due to diffusion of material in the interprecipitate liquid, in response to deposition round primary crystals and the subsequent establishment of a composition gradient (cf. Hess, 1939; Brown, unpublished thesis, 1954). Rocks in which the only minerals to participate in the layering are diopside and bytownite are found in Rhum, though subordinate to the rest. One in which the grain-size and general distribution of the minerals is con-

parable with that of the calc-silicate hornfels (Wells, 1951, fig. 11) is shown in fig. 1. The fine grain-size of the Rhum rock is attributed to granulitization through slumping, whereas in the hornfels it may be due to granulitization by re-heating.

TABLE I. Analysis of the diopside-bytownite inclusion from Ardnamurchan compared with analyses of igneous and sedimentary rocks.

	1.	2.	3.	4.
SiO_2 ...	46·26	46·39	48·92	48·12
Al_2O_3 ...	24·18	26·34	25·00	12·80
Fe_2O_3 ...	1·38	2·02	0·48	1·60
FeO ...	3·96	3·15	0·75	3·25
MgO ...	3·58	4·82	4·30	2·55
CaO ...	17·67	15·29	18·01	10·77
Na_2O ...	1·54	1·63	1·65	0·60
K_2O ...	0·09	0·20	0·09	3·60
H_2O+ ...	0·73	0·48	0·19	3·25
H_2O- ...	0·19	0·10	0·15	1·70
TiO_2 ...	0·16	0·26	0·19*	0·78
P_2O_5 ...	nil	trace	nil	0·65
MnO ...	trace	0·14	0·05	0·09
Cr_2O_3 ...	n.d.	trace	0·22	—
CO_2 ...	nil	—	n.d.	9·19
Others ...	—	—	—	1·37
	99·74	100·82	100·00	100·32

1. Banded calc-silicate hornfels, Sanna Point, Ardnamurchan. Analyst, W. H. Herdsman. (Wells, 1951, table III.)
2. Olivine-gabbro of Cuillin Hills, Isle of Skye. Analyst, W. Pollard. (Harker, 1904, p. 103.)
3. Layered allivalite (H5049) from the Isle of Rhum, recalculated to 100 % after subtracting 20 % olivine. Analyst, G. M. Brown.
4. Marine marlstone (calcareous shale), Ordovician. Analyst, D. Schaaf. (Pettijohn, 1949, table 84.)

Though a pyroxene-felspar accumulation has not been analysed from Rhum, a neighbouring olivine-pyroxene-felspar accumulation has. As the olivine from the rock has also been analysed, the composition of a pyroxene-felspar accumulation has been obtained by subtraction of the composition of an appropriate amount of olivine from the rock analysis. This estimated composition (table I, column 3) compares closely with that of the banded pyroxene-felspar-rock from Ardnamurchan (column 1). Differences are probably due to the absence of epidote and scarcity of ore in the Rhum specimen, and consequent greater SiO_2 content, and to the more ferriferous character of the Ardnamurchan pyroxene. The ore and clinopyroxene in the Rhum specimen are chromiferous, and it would be of interest to know the Cr_2O_3 content of the Ardnamurchan hornfels.

To derive the banded granular hornfels inclusions of Ardnamurcha from sedimentary rocks, as suggested by Wells, would require mu metasomatic replacement as well as complete recrystallization. On th other hand, there are varieties of layered ultrabasic or basic igneou

FIG. 1. Photomicrograph of a banded diopside-bytownite-rock (H 5626) from the ultrabasic layered series (unit 10), Hallival, Isle of Rhum. ×11.

rocks, such as found in Skye and Rhum, from which the hornfels could be derived by simple thermal metamorphism. It seems reasonab to suggest that such rocks exist at some level beneath the Ardnamurcha layered hypersthene-gabbro.

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The occurrence of palygorskite, near Ipswich, Queensland.

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Introduction.

In the course of an investigation on the determination of soil carbonates a sample of dolomite, from the Ibis dolomite quarry, M Flinders, Queensland, was examined by X-ray diffraction and found t contain palygorskite.[3] As this appears to be the first recognition of th occurrence of the mineral in Australia and as it has a number of com mercial uses (e.g. as a drilling mud, catalyst, decolorizer, and absorbent further work was undertaken.

Geology of the area.

Jensen (3) has described the development of the igneous rocks in th area, with special reference to the Flinders and Fassifern volcanoes. general description of the Moreton district is given by Jones (4), bu with little direct information on the Flinders dolomite. David (5) refe to the area and describes the Redbank series between Ipswich an Brisbane within an area of 18 miles by 12, as 'outcrops of freshwate beds . . . consisting of 300 feet of clays, shales and sandstone overla by 500 feet of basalt. . . . Just east of Ipswich it is overlain . . . by th (Tertiary) Silkstone series of mudstones, shales and sandstones, dol mitized and silicified limestones with *Planorbis* and marly clays, wit two interbedded flows of basalt; the total thickness is about 400 feet

It seems, therefore, that the dolomite found in the Ipswich area wa deposited in fresh-water lakes during Tertiary times. The occurrenc of palygorskite in the area is in keeping with those previously reporte in the U.S.A. at Attapulgus (6), in France (7), and South Africa (8 where the palygorskite is associated with limestones of lacustrine origi

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[3] Palygorskite and attapulgite are synonymous. Palygorskite is used here as has historic precedence (1, 2).

Description of the quarry.

The Ibis dolomite quarry, Mt. Flinders (grid reference 857499, Flinders map, 1 mile series) is situated in the area covered by the Silkstone series. In the vicinity of the quarry the upper portions of the hillocks are composed of dolomite, basalt occurring farther downhill. Basalt also occurs as a capping on the tops of some of the hills. The dolomite is quarried after the removal of the shallow overlying black soil. In the quarry the dolomite occurs as massive blocks with horizontal and vertical cracks. Throughout the deposit there occur horizontal and vertical bands, 4–12 inches thick, of a pinkish-grey, shaly clay (palygorskite), in which hard brownish cores (mainly sepiolite) are distributed irregularly. At the level of the floor of the quarry a thicker deposit, 2 feet deep, of greenish clay occurs (this may be partly downwash from the quarry face) overlying a similar but pinkish clay which is at least 1½ feet thick (both clays contain palygorskite, montmorillonite, and dolomite).

Samples were taken from the main quarry only, but a visit to several adjacent hills which were being quarried indicated that they were similar to the main site.

Mineralogy of the Mt. Flinders deposits.

1. *Dolomite.*—X-ray diffraction analyses indicated that the large blocks from the quarry were mainly dolomite with a palygorskite impurity. Treatment of the dolomite with 0·1N HCl left a residue which gave an X-ray diffraction pattern in very good agreement with that given by Bradley (9) for pure palygorskite.

2. *Palygorskite.*—X-ray diffraction analysis indicated that the shaly clay occurring as bands was very pure palygorskite. The green and pink clays from the floor of the quarry each contained palygorskite and montmorillonite with a little dolomite.

A chemical analysis of the clay separate (less than 0·002 mm.) of the pure palygorskite is given in table I. It is almost identical with South African palygorskite (8), but differs from most other published analyses in that there is a little less alumina but correspondingly more magnesia. No calcium was found and this is probably an indication of the high purity of the material analysed. During the separation of the clay it was treated with 0·2N HCl, so that any carbonate would have been removed. Most published analyses show several per cent. CaO, but since calcium probably cannot occur in the lattice of the mineral and

since only about 1 % CaO can be accounted for as exchangeable cation any excess over this is most likely due to contamination.

TABLE I. Chemical analyses of palygorskite and sepiolite.
(Percentages calculated on oven-dry basis.)

	1.	2.	3.	4.	5.	6.
SiO_2	59·09	61·60	59·02	75·50	61·17	59·75
TiO_2	0·99	—	0·66	0·14	0·23	0·48
Al_2O_3	6·84	6·82	9·64	1·06	1·69	0·30
Fe_2O_3	4·21	0·87	3·70	1·84	2·92	—
FeO			0·25			
CaO	(< 0·01)	0·67	2·22	0·51	0·80	0·66
MgO	14·12	14·22	9·96	12·61	20·01	26·76
H_2O+	14·18	14·16	11·98	8·08	12·82	11·76
&c.	—	—	2·64	—	—	0·42
Total	99·43	98·34	100·07	99·74	99·64	99·92
H_2O-	8·00	—	9·12	7·70	11·68	8·18
Exchange capacity m.e./100 g. ...	5·74	20	21	—	—	—

1. Palygorskite, Mt. Flinders, Queensland, $< 2\mu$.
2. ,, Dornboom, South Africa. H_2O given as ignition loss. (Heystek and Schmidt, 8.)
3. ,, Attapulgus, Georgia, U.S.A. (Bradley (9) recalculated to oven-dry basis.)
4. Sepiolite, Mt. Flinders, Queensland.
5. ,, Mt. Flinders. Calculated, deducting chert, assuming an average of 61 % SiO_2 for sepiolite.
6. ,, Yavapai County, Arizona. (Kauffman (10), recalculated to oven-dry basis.)

Total exchange capacity determinations were carried out on acid-washed samples by an equilibrium method using normal ammonium acetate at pH 7·0. It is seen from table I that the exchange capacity is appreciably lower than that usually quoted in the literature for this mineral. This is thought to be due partly to clumping of the sample in the reagent, as saturation of the raw material (containing 72 % of the < 0·002 mm. fraction) under vacuum to displace all entrapped air gave a value of 7·34 m.e./100g. This is still greatly below the accepted exchange capacity and the discrepancy has yet to be explained. One sample from the floor of the quarry gave a value of 34·15 m.e./100g. but this material is known to be contaminated with montmorillonite.

The palygorskite clay was heated at 100° C. intervals to 1000° C. and diffraction patterns were obtained for each temperature. The diffraction data agreed, in general, with those of Longchambon (11, 12). The 10·5 Å. line became faint at 550° C. when a 9 Å. line began to appear. The mineral was converted to α-cristobalite and enstatite at 850° C.

3. *Sepiolite.*—The hard brownish cores in the shaly clay were identified by X-ray diffraction as sepiolite with some chert and a little palygorskite. The cores were covered by a crust intermediate in properties between the brown core and the clay, and this contained about equal amounts of palygorskite and sepiolite with a little chert.

The brown cores were hard and dense and this departure from the normal physical properties of sepiolite is to be explained by its impregnation with chert. A chemical analysis of the material of the core is given in table I. If sepiolite is considered to contain 54 % SiO_2, then the sample contains 34 % free SiO_2.

X-ray diffraction patterns of heat-treated samples were in reasonable agreement with the results given by Migeon (13). The 12 Å. line of sepiolite disappeared at 850° C. and at that temperature the mineral changed to enstatite and α-cristobalite. Migeon did not detect the cristobalite phase until 1100° C. in the heated sepiolite. As the sepiolite found in the quarry was intimately mixed with chert, the temperature at which the α-cristobalite phase first appears is difficult to determine.

4. *Chert.*—Chert was a contaminant of most of the samples examined and was identified by the strong diffraction line at 4·1 Å and 2·5 Å. When pure it gives a diffraction pattern similar to but not identical with that of β-cristobalite (14). Gruner (15) discusses the occurrence of cristobalite in bentonites and fuller's earth.

5. *Soil.*—A rendzina soil overlies the dolomite outcrop at this quarry. An examination of the clay fraction of the soil showed palygorskite with small amounts of sepiolite, dolomite, calcite, quartz, chert, and montmorillonite. Palygorskite has been observed as a clay mineral of brown desert soils in Syria (16) and terra rossa soils in the south of France (7), but there was no indication in these reports as to whether the mineral was a constituent of the underlying limestones. The presence of palygorskite in the clay fraction of this soil probably indicates relatively mild pedogenic processes leading to the genesis of the rendzina.

Mineralogy of the Queen's Park bore.

To determine the extent of the palygorskite occurrence, other dolomites from the area were examined. Through the courtesy of the Queensland Geological Survey, samples from a deep bore, NS2/1944 (17), at Cribb's estate (NW. corner of portion 131, Queen's Park, Ipswich), were made available for study. This site is about 17 miles NNE. from the Ibis quarry. The bore was put down to a depth of 903 feet, and basalt occurred at the following depths: 125–130, 235–283, 333–388,

and between 414 and 760 feet, interlayered with soft brown mud. Between these flows dolomitic clays were found. The following gives the results of the X-ray analysis of the samples which were available.

120 feet: dolomite and montmorillonite with traces of palygorskite and kaolin.
209, 213, 215, 218 feet: palygorskite and dolomite.
220 feet: palygorskite, dolomite, and montmorillonite.
300, 308, 315 feet: palygorskite and dolomite.
384 feet: dolomite and palygorskite.
393 feet: dolomite, sepiolite, and trace of palygorskite.
790 feet: quartz and montmorillonite.
805 feet: quartz, montmorillonite, and kaolin.

Taking local variations into account, the dolomite deposits down to 393 feet appear to be very similar to those found in the Flinders quarry. It therefore appears that palygorskite and sepiolite may occur fairly widely in limestones of the Ipswich area.

Origin of the palygorskite.

Dunstan (18), in a report on the suitability of Flinders dolomite for cement manufacture, considered that the dolomite deposit was formed by a combination of lime from local calcareous sandstone, with magnesia from decomposed basalt. It is now considered, however, that the sandstone is non-calcareous. Nevertheless, there seems no reason why both the calcium and magnesium could not have come from the weathering of the basalt. The tropical weathering of basalt consists largely in the removal of alkali and alkaline earth metals and silicon. Iron and aluminium, as shown by their concentration in tropical soils forming from basalt, tend to be retained. In the present instance, the calcium, magnesium, and silicon from the basalt appear to have been deposited in lakes as dolomite, sepiolite, and chert. Subsequent additions of aluminium probably altered much of the sepiolite to palygorskite.

Longchambon (19) has observed that palygorskite appears to be formed by the alteration of pyroxenes and amphiboles, and in a later paper (12) he proposed that palygorskite is derived from sepiolite by the isomorphous replacement of magnesium by aluminium. Although palygorskite and sepiolite appear to be related they are not isostructural, and more work, particularly on the structure of sepiolite, will be necessary before the relationship of these two minerals is understood. Heystek and Schmidt (8) suggest that, in the Transvaal deposit, palygorskite

has been derived from montmorillonite. There is no evidence at the Mt. Flinders deposit supporting this hypothesis and it appears that, in the Ipswich area, palygorskite is formed from sepiolite.

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Rammelsbergite from the southern uplands of Scotland.

(With Plate XVI.)

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DURING an investigation of the mineralization of the Leadhills-Wanlockhead lead and zinc mining district, rammelsbergite ($NiAs_2$) was identified as an associate of niccolite (NiAs), reputed to have come from no. 4 level on the west branch of the New Glencrieff vein. The identification was confirmed on further material collected from the dumps at the Glencrieff mine, Wanlockhead, Dumfriesshire, and on specimens from the Scottish Mineral Collection (nos. 1952.5.18; 20; 21).

The niccolite from the Glencrieff mine,[1] with which the rammelsbergite is invariably associated, has a rounded or 'pseudo-conglomeratic' form, and is in contact with brecciated fragments of the country-rock, a fine-grained, shaly greywacke. Niccolite from Cassencarrie, Kirkcudbrightshire, has a similar form.

The rammelsbergite borders and veins the niccolite, the junction of the two minerals being irregular but clearly defined. In polished section the rammelsbergite is seen to be anisotropic, and to be of a strong white colour, against which galena appears light grey. The hardness of the rammelsbergite is comparable with that of niccolite.

Although the maximum width of the rammelsbergite was only 0·2 mm., successful etch tests were carried out. With nitric acid the mineral effervesced and was stained black, the reaction commencing only when the niccolite had ceased to react with the acid. The mineral was slowly stained light brown with ferric chloride, whilst no reaction was given with mercuric chloride, hydrochloric acid, potassium cyanide, or potassium hydroxide.

[1] R. Brown, More about the mines and minerals of Wanlockhead and Leadhills. Trans. Dumfries. and Galloway Nat. Hist. Antiq. Soc., 1927, vol. 13 (for 1925-26), pp. 58–79 (p. 75). [M.A. **4**–468.]

The above description applies either to rammelsbergite or pararam melsbergite,[1] but the presence of the former was confirmed by the X-ra diffraction pattern, which compares with the data for rammelsbergi published by Peacock and Dadson (1940). It was not practicable t separate the rammelsbergite from the niccolite for chemical analysis spectrographic analysis of the mixed material showed Ni and As as t major elements, with traces of Co, Sb, Bi, Sn, &c.

TABLE I. X-ray powder data for rammelsbergite.

1.		2.		1.		2.	
d (Å.).	Int.	d (Å.).	Int.	d (Å.).	Int.	d (Å.).	Int.
3·66	vw	3·68	m	1·58	w	1·593	m
3·01	w	3·02	vw	1·52	vw	1·530	m
2·84	vs	2·85	s	1·43	m	1·439	s
2·56	vs	2·56	s	1·37	vw	1·373	vw
2·47	s	2·47	s	1·22	w	1·236	m
2·38	vvw	2·40	vw	1·15	w	1·157	m
2·20	vw	2·21	w	1·12	vvw	1·121	w
2·02	w	2·02	w	1·09	vvw	1·096	w
1·87	s	1·871	s	1·06	vvw	1·071	w
1·80	w	1·796	w	1·05	vw	1·052	w
1·76	w	1·763	m	1·03	vw	1·037	w
1·69	m	1·690	m	1·02	vw	1·024	m
1·62	w	1·635	m	1·01	vw	1·011	m

1. Rammelsbergite from Glencrieff mine, Wanlockhead, Dumfriesshire. Filtere Cu–$K\alpha$ radiation.
2. Rammelsbergite from Eisleben, Thuringia. Unfiltered Cu radiation (β diffrac tions omitted). Data by M. A. Peacock and A. S. Dadson, Amer. Min., 194 vol. 25, p. 570. [M.A. 8–3.]

The paragenetical relationships of rammelsbergite, niccolite, an galena were ascertained from polished sections. The rammelsbergit both borders and veins the niccolite: the niccolite-galena junction i irregular, and occasional small inclusions of galena are present in th margin of the niccolite. It would appear, therefore, that the order o deposition was galena, niccolite, and rammelsbergite, and that th rammelsbergite was deposited after the niccolite had come into contac with the galena. Ankerite is earlier and quartz later than the metall minerals (pl. XVI).

The only previous record of rammelsbergite in the British Isles wa given by Goodchild,[2] who pointed out that on one of the tickets of th

[1] W. Uytenbogaardt, Tables for microscopic identification of ore mineral Princeton and London, 1951. [M.A. **12**–6.]

[2] J. G. Goodchild, supplement in M. F. Heddle, The mineralogy of Scotlan 1901, vol. 2, p. 195. [M.A. **3**–24.]

Scottish Mineral Collection (no. 602.3) Dr. Heddle had stated that rammelsbergite occurred with niccolite at 'Menimuir Burn, Cassencarrie'.

Further investigation of the Scottish Mineral Collection specimens revealed the presence of rammelsbergite in three instances, viz. no. 71.4, Cassencarrie, Kirkcudbrightshire; no. 602.3, Hilderston, Linlithgowshire (locality queried); and no. 602.4, Cassencarrie (locality queried). In all three cases the rammelsbergite is associated with niccolite, and has the same relationship towards it as has been described above.

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EXPLANATION OF PLATE XVI.

Rammelsbergite (r), niccolite (n), and galena (g), from Glencrieff mine, Wanlockhead, Dumfriesshire. The gangue mineral at the top is ankerite, and across the middle quartz.

A. Unetched, reflected light, ×70.

B. Galena and niccolite etched with nitric acid to display the rammelsbergite bordering the niccolite. Reflected light, ×70.

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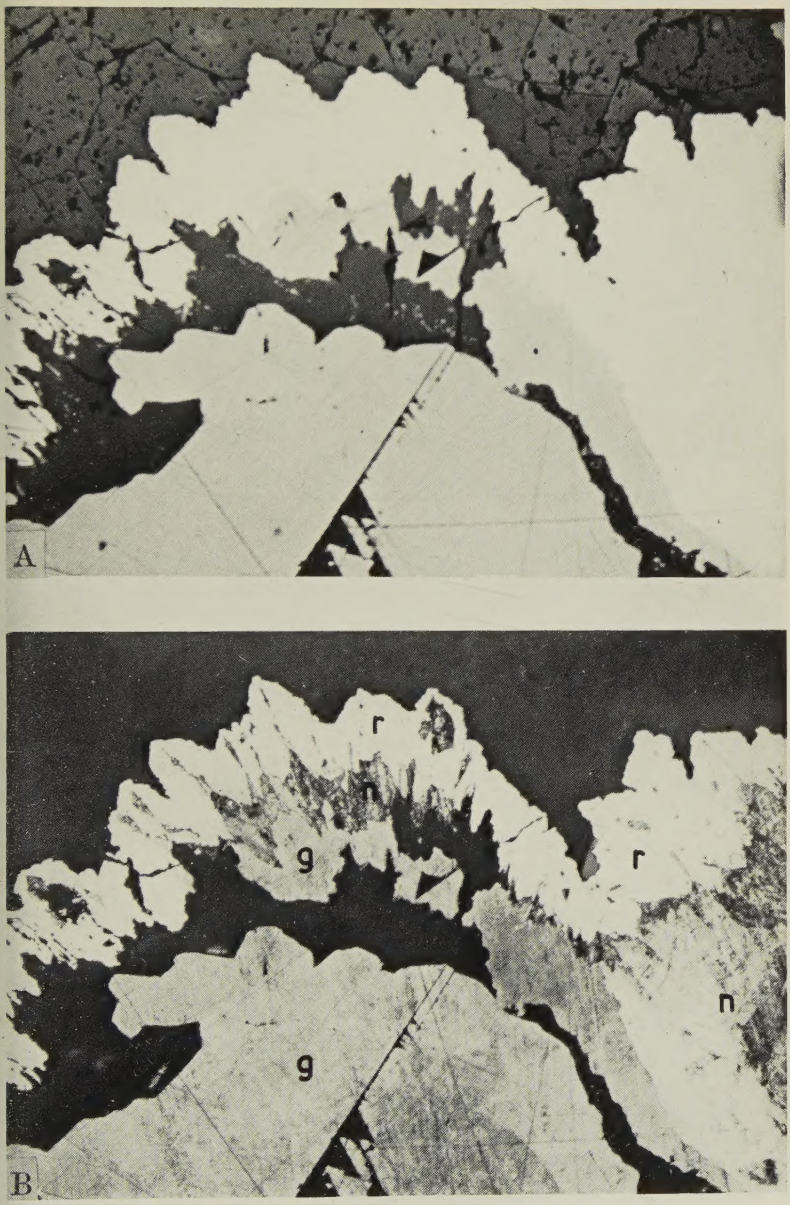

A. K. TEMPLE: PHOTOMICROGRAPHS OF RAMMELSBERGITE, WANLOCKHEAD, SCOTLAND.